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VARIATIONAL PRINCIPLES IN THE COLLISION THEORY

Yu. N. Demkov

Translation of "Variatsionnyye printsipy v teorii stolknoveniy," Gosudarstvennoye Izdatel'stvo Fiziko-Matematicheskoy Literatury, Moscow, 1958.

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By Yu. N. Demkov

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TRANSLATOR'S NOTE

The following errors have been noticed in the Russian text of this paper:

Page 14 (Russian text)

Equation (7) reads

$$\Psi = F\,(\vec{r}_0)\ \psi\ (\vec{r}_1, \cdots \vec{r}_n).$$

should read

$$\Psi = F\,(\vec{r}_0)\ \psi\ (\vec{r}_1, \cdots, \vec{r}_n)$$

Page 15 (Russian text)

Equation (9) reads

$$U = -\frac{n}{r} + \int \cdots \int |\psi\ (r_1, \cdots r_n)|^2 \sum_{i=1}^{n} \frac{1}{|r - r_i|}\, d\tau_1 \cdots d\tau_n.$$

should read

$$U = -\frac{n}{r} + \int, \cdots, \int |\psi\ (r_1, \cdots, r_n)|^2 \sum_{i=1}^{n} \frac{1}{|r - r_i|}\, d\tau_1, \cdots, d\tau_n.$$

Page 29 (Russian text)

Equation (11): the equation number is omitted.

Page 85 (Russian text)

Equation (1), last term reads:

$$= St\left\{\tilde{f}_{ij}\ (v_1, -v_2) + \frac{k_i}{4\pi}\iint \Psi_2^{(j)}\ L\ \Psi_1^{(}\ d\tau_1\ d\tau_2\right\}.$$

should read

$$= St\left\{\tilde{f}_{ij}\ (v_1, -v_2) + \frac{k_i}{4\pi}\iint \Psi_2^{(j)}\ L\ \Psi_1^{(i)}\ d\tau_1\ d\tau_2\right\}.$$

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

FOREWORD /7

From a large number of problems related to variational principles in collision theory, only a few have been selected for this book. First of all prime attention is given to stationary problems and non-stationary problems have been almost entirely omitted. Although the specific transition from a non-stationary to a stationary problem is essential for substantiation of variational principles, nevertheless the variational principles, as such, might be formulated without this transition and all concrete calculations can always be reduced to stationary problems. The specific problems which are being investigated here are entirely non-relativistic. The application of variational principles in relativistic quantum mechanics and field theory are not examined here at all, although many results which were obtained in this book are of the same general character. Finally, for the most part, various principal problems which are related to variational principles are being analyzed in this book. Numerical calculations are given mainly for the purpose of illustrating certain general states and methods. By the same token it is emphasized that variational principles are suitable, not only in the case of numerical calculations, but also for the purpose of obtaining many general results which are at times difficult to derive by other means.

Instead of formulating the variational principles and their after effects in the most general form by utilizing the so-called formal theory of scattering, this book will present concrete problems which are sufficiently general so that the generalization into complicated /8 problems would not present any difficulties in principle. Therefore, the conclusions drawn are general in nature and are not compromised by approximations. Such a method of reporting is noticeably more awkward and possibly less exquisite; however, I hope this method will make it easier to read the book.

The mathematical conclusions are stated with a degree of rigor normally considered to be sufficient in physical discussions. Many reservations as to the conditions which should be placed on the functions, operators, etc., are avoided and are not investigated on purpose, with the exception of those cases which represent a special interest.

Some of these results are recent and are being published here for the first time. Up to the present time summaries and monographs on the given problem were absent in the literature. In the widely known monograph on the collision theory by Mott and Massey, only two pages in their second edition were dedicated to variational principles. Therefor, this book can be considered as a supplement to the monograph by Mott and Massey.

In order to read the book it is necessary to have a knowledge of non-relativistic quantum mechanics including fundamentals of the collision theory: the statement of the problem, the phase method, etc.

The material in this book is divided as follows:

In the first chapter a short review on the application of variational principles in quantum mechanics is given. Then the formulation of the variational principle for various, increasingly complicated problems in the collision theory (a one dimensional equation of phase; a general problem on elastic scattering of particles by a force field; elastic and inelastic collisions for the problem of many bodies) is considered. Problems are discussed on broadening of the class of permissible variations so as to substantiate the possibility of application of the variational principle in those cases when the wave functions of the colliding particles are only approximately known.

In the second chapter a relation between the various formulations of the variational principle is established (the variational principles by Hulthen, Kohn, and Schwinger). In this paper the relation of the variational principle with the excitation theory utilizing the Born /9 method, the method of wave excitation, the method of a self-adjusted field, etc., are examined. Various versions of direct methods of phase calculation are discussed, and results obtained with the help of variational methods for electron scattering on hydrogen are analyzed. It is proven in particular that there exists an infinitive succession of variational principles, in which the first two places are occupied by the variational principles by Kohn and Schwinger.

In the third chapter those general properties which should be satisfied by the amplitude of scattering and the effective cross-section are discussed. It is proven that these properties (the correlation of unitarity and the principle of separate equilibrium) follow from the symmetry of the basic functional, which is being considered in the variational principles, by the relation toward the permutation of the wave function at the initial and final state. In this chapter the variational principle which is connected with the correlation of unitarity is formulated; also examined is the relation between the elastic and inelastic cross-section of scattering. In conclusion the properties of symmetry and the variational principle for the matrix of transition in a non-stationary problem of quantum mechanics are considered.

In the fourth chapter formulae which are analogous to the virial theorem in problems of a discrete spectrum are derived for various cases by scale variation. Certain results of these formulae are also studied.

The logical relation of the various sections in this book is such that any of the Chapters II, III, IV can be read directly after reading Chapter I. The same pertains also to the various sections in Chapter II, with the exception of Sections 10-11, and also Sections 13-14, which are closely related with each other.

The contents of a large part of this book were reported and discussed at seminars of the Department of Theoretical Physics at the Leningrad University. I would like to express my gratitude to all associates of this department for the attention and interest which they have displayed; and most of all I would like to express my thanks to the department head, V. A. Fok, as well as N. G. Veselov, Yu. V. Novozhilov, M. I. Petrashen, and P. P. Pavinsky for their valuable remarks. I /10 am also very much obliged to F. P. Shepelenko who assisted me in writing Section 12 and L. D. Faddeyev for the detailed evaluation of problems related to the deriviation of the Newton formula from the virial theorem in Section 31. In addition, almost all sections of this book were evaluated in detail at meetings with G. F. Drukarev to whom I must express my special gratitude.

CHAPTER I

/11

FORMULATION OF THE VARIATIONAL PRINCIPLE

§1. Statement of the Problem on the Collision of Electrons with Atoms and Calculations Which Were Made Before Variational Methods Were Available

If we have an n-electron atom and a cluster of non-interacting electrons which bombard that atom, then such a system is characterized by the wave function which should satisfy the Schroedinger equation *

$$\left[-\frac{1}{2}\nabla_0^2 + H_0(\vec{r}_1, \cdots, \vec{r}_n) + \mathcal{U}\right]\Psi(\vec{r}_0, \vec{r}_1 \cdots \vec{r}_n) =$$

$$= H\Psi(\vec{r}_0, \vec{r}_1, \cdots, \vec{r}_n) = E\Psi. \qquad (1)$$

Here $\vec{r}_0$ are the coordinates of the bombarding electron; $\vec{r}_1, \cdots, \vec{r}_n$ are the coordinates of the atomic electrons; H_0 is the energy operator of the n-electron atom; $\mathcal{U}$ is the interaction operator between the electron and the atom; $\mathcal{U} = \sum_{i=1}^{n} \frac{1}{|\vec{r}_0 - \vec{r}_i|} - \frac{n}{r_0}$. (Atomic units are used in this case, as well as throughout the entire book.) At large r_0 the wave function should have an asymptotic form

$$\Psi(\vec{r}_0, \vec{r}_1, \cdots, \vec{r}_n) \sim e^{ik\vec{v}\cdot\vec{r}_0}\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n), \qquad (2)$$

where k is the wave number and $\vec{v}$ is a single vector which characterizes the direction of the bombarding electrons. $\psi(\vec{r}_1, \cdots, \vec{r}_n)$ /12 satisfies the equation

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*In this book a consecutive numeration of formulas inside of each section is adopted. When referring to a formula in another section the number of this section will be indicated before the number of the formula. For instance (1.3) is formula (3) Section 1. If a reference is made to a formula in the same paragraph, then the section number is not indicated.

$$H_0\psi = \mathcal{E}\psi, \tag{3}$$

and is a wave function of the basic or excited state of the atom. The total energy E in (1) consists of the energy of the atom $\mathcal{E}$ and the energy of the bombarding electron

$$E = \mathcal{E} + \frac{k^2}{2}. \tag{4}$$

If we take into consideration the requirement for anti-symmetry of a full wave function (including the spin function), then it is necessary to complicate formula (2) by correspondingly symmetrizing the right part.

However, in the case of a well-defined solution to equation (1) the boundary condition (2) is still insufficient. In addition, we should also strive for fulfillment of the so-called emission principle. This means that in all parts of configurational space (that is, during the increase of any of the r_j) only divergent scattered waves in an asymptotic resolution of the function Ψ should be contained, in addition to the basic term. This condition is placed only on those terms of an asymptotic solution which decrease inversly proportional to the first power of the r-distance from the origin of the coordinates (center of atom). The terms which decrease more rapidly than r^{-1} are not subjected to any limitations. Since stationary problems will henceforth be examined almost exclusively, it should be especially stipulated that by the expression "wave direction" we will understand the direction of its wave vector $\vec{k}$. Thus, the expression e^{ikr}/kr gives a spherical symmetrical divergent wave, and e^{-ikr}/kr gives a convergent wave. We will not concern ourselves in detail here with the nature of the emission principle, especially since in quantum mechanics this principle is of the same nature as in classical physics. In order to accomplish this, it would have been necessary to pass on toward non-stationary problems. We will only mention here that actually /13 the principle of emission is equivalent to the requirement that the scattering processes should satisfy the condition of causality; that is, that the event-cause should always precede the event-consequence.

In the simplest case, when an atom is in its fundamental state, the energy of the bombarding electrons is insufficient to cause excitation of the atom and we do not consider the properties of symmetry, the asymptotic form of the wave function will be

$$\Psi \sim \begin{cases} \left[e^{ik\vec{v}\cdot\vec{r}_0} + f(\vec{v}, \vec{n}_0) \frac{e^{ikr_0}}{kr_0} \right] \Psi(\vec{r}_1, \cdots, \vec{r}_n), \; r_0 \to \infty, \\ g_i(\vec{v}, \vec{n}_i) \frac{e^{ik\vec{r}_i}}{kr_i} \Psi(\vec{r}_1, \cdots, \vec{r}_{i-1}, \vec{r}_0, \vec{r}_{i+1}, \cdots, \vec{r}_n), \\ r_i \to \infty \; (i = 1, 2, \cdots, n). \end{cases} \quad (5)$$

Here $\vec{n}_i = \vec{r}_i/r_i$; and f, the amplitude of elastic scattering as well as g_i, the amplitude's exchange scattering, are the complex functions which are determined identically during this solution of equation (1). Through these values the effective cross-section is simply expressed. For instance, the differential effective cross-section of elastic scattering (without an exchange) will have the following form

$$\sigma(\vec{v}, \vec{n}) = \frac{1}{k^2} |f(\vec{v}, \vec{n})|^2. \quad (6)$$

If we take into consideration the symmetry of the full wave function Ψ, then formula (5) should be symmetrized, the elastic scattering and the exchange become indistinguishable, and the exchange amplitudes g_i will be included in the expression for the effective cross-section of elastic scattering. In the case of large energy of the bombarding electrons, there will appear in (5) still other terms in the asymptotic solution which will correspond to the inelastic processes and ionization of the atom.

Such a statement of the problem is completely rigorous* and we have no doubt at the present time that the results obtained during its accurate solution would have been in complete agreement with the experiment. However, even in the simplest case of a collision between /14 electrons and an atom of hydrogen it is very difficult to solve equation (1). Therefore, it is necessary to introduce various simplifying assumptions. In particular, an elastic as well as inelastic collision can be comparatively easily investigated if we assume that the interaction energy $\mathcal{U}$ in equation (1) is small in comparison with the kinetic energy of the bombarding electrons. This assumption is true for electrons

*So far we are disregarding the relativistic affects, the magnetic interaction of the electrons, etc.

with an energy on the order of hundreds of electron volts and higher. In that case it is possible to take advantage of the excitation theory, and in the first approximation we obtain a comparatively simple expression for the amplitude of scattering f and the effective cross-section σ. It is also easier to measure the cross-section σ for rapid collision than in the case of a slow collision. A comparison of results from application of the excitation theory (the Born method) and the experimental data yield good agreement (see, for instance, Mott and Massey, Ref. 1, Chapter IX).

Within the framework of the first approximation and the theory of excitation, it is possible to consider the electron exchange; however, the calculation of polarization of the atom by the bombarding electron, as well as the distortion of the electron wave requires a transfer to higher order approximations, which is very cumbersome and non-effective. In the case of slow collision, it is necessary to utilize other methods, since all these factors become, generally speaking, essential.

A second assumption which corresponds to the Hartree approximation, is contained in the fact that the wave function can be presented approximately as follows:

$$\Psi = F(\vec{r}_0)\ \psi(\vec{r}_1, \ldots \vec{r}_n). \tag{7}$$

We thereby assume that the function ψ is known to us from other calculations. Then, for the wave function of the bombarding electron F we obtain the equation*

$$\left[-\frac{1}{2}\nabla^2 + U(r)\right] F = \frac{k^2}{2} F, \tag{8}$$

where U (r) has the following form /15

$$U = -\frac{n}{r} + \int \cdots \int |\psi(\vec{r}_1, \cdots \vec{r}_n)|^2 \sum_{i=1}^{n} \frac{1}{|\vec{r} - \vec{r}_i|} d\tau_1 \cdots d\tau_n. \tag{9}$$

Consequently, the atom is substituted in such an approximation by an effective potential field. The potential U might be calculated if a calculation of the wave function for the given atom was conducted (for

*The problem on the derivation of this equation is discussed in detail in Chapter II.

instance, by using the method of a self-coordinated field), or this atom might be substituted by a much rougher potential, derived by the Thomas-Fermi method.

Within the framework of such an approximation the exchange and polarization of atomic electrons by the following wave is not considered. It is also obvious that it is impossible to solve the problem on inelastic scattering with this method. However, in spite of the crudeness of this method, a fair agreement with experimental data was obtained in the case of complex atoms, even when used in the capacity of U (r), the Thomas-Fermi potential.* Therefore, the problem of the scattering of electrons by a central force field is essential in the theory of slow collisions. However, in certain cases (for instance, during collisions with atoms of helium and hydrogen) it is necessary to take into consideration the electron exchange, that is the symmetry of the coordinate wave function. The simplest way for doing this is by correspondingly symmetrizing the expression of (7). Then we will obtain for the function F a more complicated integral differential equation, which will contain characteristic exchange terms. Such an equation was solved, for instance, by Morse and Allis (Ref. 3) for the collision of electrons with atoms of hydrogen and helium. The calculations are quite complicated. The results proved to be in much better agreement with experimental data than those which were obtained without the consideration of exchange, particularly at low energies.

The calculations of the atom's polarization is an even more difficult problem than the calculation of exchange and until recently only one paper dealing with this problem was available (Ref. 4).

If we compared the problem on collision of electrons with /16
atoms, for instance, with the problem on the calculation of energy levels of multi-electron atoms [where it is necessary to solve actually the same equation (1)] , then we will see that in the first case much less was done and the results are considerably less reliable than in the second case. This can be explained on one hand by the fact that there is much less experimental data on the effective cross-sections than on atomic spectra. Therefore, a comparison of theory and experiment can successfully be conducted only in rare cases, and the problem of the accuracy of the methods applied in the collision theory often remains questionable. On the other hand, the method of calculation in the collision theory is less developed than the method of calculation for related states and the calculations themselves considerably less cumbersome. Particularly in the collision theory, no one succeeded, until recently, in utilizing the

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*See Mott and Massey (Ref. 1) Chapter IX, X, and also Gombash (Ref. 2), Section 29. This paper contains references to original work.

variational methods which have played an extremely important role in atomic calculations of related states.

§2. Variational Principles For The Problems Of A Discrete Spectrum

Variational methods have been used in quantum mechanics since its very beginning. In the first papers by Schroedinger the problem of finding the energy levels of a particle in a potential field was formulated as a problem of specific values. The variational principles for this type of problem were formulated in mathematics a long time before the appearance of quantum mechanics. Also formulated were the so-called direct methods (the Ritz method), which have made it possible to approximately calculate the specific values as specific functions based on their extreme properties.

A large number of concrete calculations of the energy levels for atoms and molecules was made with the help of the Ritz method. Among these should be noted the works by Hylleraas (Ref. 5) (Calculations of the Atoms of Helium) and the works by James and Coolige (Ref. 6) (Molecules of Hydrogen). The discrepancy between the experimental data and the figures which were obtained in these calculations was within the limits of experimental error and; thus, the complete applicability /17 of quantum mechanics towards atoms with several electrons and molecules was confirmed.

In addition to the calculation of the energy levels, variational methods can be utilized for the calculation of such magnitudes as the polarizability of atoms and molecules, the entire magnetic susceptibility, etc. In particular, the calculations of the polarizability of the most simple atoms (Ref. 7) and molecules (Ref. 8), which were conducted with such a method, have led to good agreement with the experiment.

In 1930 the variational principle was utilized by V. A. Fok (Ref. 9) for substantiation of the method of the self-aligned field by Hartree and for the formulation of the more accurate method, the Fok method, in which the symmetry of the wave function (electron exchange) is taken into consideration. It is easy to extract from the variational principle the basic equations of the Thomas-Fermi method, the equations of the excitation theory, etc. Finally, as was proven by V. A. Fok (Ref. 10), it is easy to prove the virial theorem with the help of the variational principle.

It is obvious from the above, that the variational principle is, on one hand, the basis for powerful calculation methods and, on the other hand, a number of important theoretical results can be easily obtained from this principle. Thus, this principle is one of the basic assertions of the quantum theory.

However, as was already mentioned, there is on hand a large group of quantum mechanical problems in which the variational principle was not formulated: those are the cases when the state of the system pertains to the continuous spectrum of the energy operator. To this type belong all problems in collision theory and particularly the problem on the collision of electrons with atoms.

§3. Variational Principles For The Problems In Collision Theory. Short Review

The first formulation of the variational principle for the simplest one dimensional problem of a continuous spectrum was given by Hulthen in 1944 (Ref. 11,12). Based on this principle Hulthen has proposed a /18 method for an approximate calculation of a radial wave function and its phase, after checking this method on simple examples.

I. E. Tamm (Ref. 13,14) formulated independently, in 1948, a variational method which is close to the Hulthen method.

In 1947 Schwinger (Ref. 15) developed a variational method which differs from the Hulthen method, based on the integral equation for wave functions.

In 1948 Kohn (Ref. 16) considerably generalized Hulthen's formulation, extending it to a general case of scattering. After that a number of papers appeared (Ref. 17) in which new variational methods were proposed; however, all these methods differed insignificantly from the two basic methods: the Hulthen-Kohn method, which is based on Schroedinger's differential equation, and the Schwinger method, which is based on the integral equation.

Proof and examples of application of these variational methods pertain mainly to the research of the phase of the asymptotic behavior of the wave function for the simplest potentials - the rectangular potential well, the Yukawa potential, etc. - and did not present any independent interest.

In 1949 the first works by Huang (Ref. 18-20) appeared, in which an attempt was made to apply the variational method to the problem on the collision of electrons with a real atomic system - the atom of hydrogen. Henceforth, the results by Huang were considerably improved by Massey and Moiseiwitsch(Ref. 21) and were further extended to other calculations - the inelastic collision of electrons with hydrogen (Ref. 22), collisions with hydrogen-like ions (Ref. 23), and finally on the elastic and inelastic collisions of electrons with atoms of helium (Ref. 24 and 25). For instance, in the case of elastic scattering on the hydrogen atom, simultaneously considering such effects as the polarization of an atom and exchange, more reliable results were obtained by the method of a self-aligned field with the exchange calculation (the Fok method) than those calculated by Morse and Allis (Ref. 3).

In addition to these papers a number of attempts were made to /19 examine the different variational methods from a single viewpoint and to give a general review of their conclusions (Ref. 26 and 27). A close relation was established between the variational methods and the excitation theory (Ref. 16, 28, and 29). Finally, it is possible to examine the variational methods from a sufficiently general viewpoint, if we introduce the concept of the collisions operator which is now being widely utilized in quantum electrodynamics and in field theory (Ref. 27 and 30).

Formulation of the variational principles for relativistic problems is present, for instance in the work by Parzen (Ref. 31) and also in the work by Yu. V. Novozhilov (Ref. 32), where problems of quantum field theory are also investigated.

Another group of variational methods based on the integral equation is less applicable for calculations of atomic collisions. Until now these variational methods were used basically for calculations of nuclear processes: for instance, for interpretational data on proton-neutron scattering (Ref. 33).

Generally speaking, all these variational methods might be used not only for the solution of quantum mechanical problems, but also for problems of electrodynamics, the theory of elasticity, and others. For instance, in the paper (Ref. 34) the variational method by Schwinger was used for the investigation of the deflection of a flat wave on a cylinder. In the paper (Ref. 35) a variational principle for an acoustical field is formulated. It might be anticipated that by utilizing these methods in the collision theory we will have in our final calculation an accuracy comparable to those now reached in the theory of atomic spectra.

§4. Hulthen's Variational Principle For A One Dimensional Equation

The Schroedinger equation for the scattering of electrons by a central force field (1.8) can be solved by resolving the wave function by partial waves - which are characteristic of the functions of the moment operator of the amount of motion m^2. We will put down the equation (1.8) in the following form* /20

$$\left[\nabla^2 + k^2 - V(r)\right] \Psi(\vec{r}) = 0, \quad V = 2U(r), \tag{1}$$

whereby

$$\Psi(\vec{r}) \sim e^{ik\vec{v}\cdot\vec{r}} + f(\vec{v}\cdot\vec{n})\frac{e^{ikr}}{kr}, \quad \vec{n} = \frac{\vec{r}}{r}. \tag{2}$$

After a resolution by spherical functions - proper functions of the operator $\vec{m}^2$ - we have (see Ref. 1, p. 38).

$$\Psi(\vec{r}) = \sum_{e=0}^{\infty} i^{\ell} e^{i\eta_{\ell}} (2\ell + 1) \frac{1}{kr} \psi_{\ell}(r) P_{\ell}(\vec{v}\cdot\vec{n}), \tag{3}$$

$$f(\vec{v}\cdot\vec{n}) = \frac{1}{2i} \sum_{\ell=0}^{\infty} (2\ell + 1)(e^{2i\eta_{\ell}} - 1) P_{\ell}(\vec{v}\cdot\vec{n}). \tag{4}$$

Here, P_{ℓ} are the Legendre polynomial , ψ_{ℓ} satisfy the equations

$$\left[\frac{d^2}{dr^2} + k^2 - V(r) - \frac{\ell(\ell+1)}{r^2}\right] \psi_{\ell}(r) = 0, \ \psi_{\ell}(0) = 0, \tag{5}$$

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*We are returning here to a more familiar definition of Ψ for the wave functions of a bombarding electron.

and the phases η_ℓ are found from the asymptotic form of ψ_ℓ

$$\psi_\ell \sim \sin\left(kr - \frac{\ell\pi}{2} + \eta_\ell\right). \tag{6}$$

Thus, the solution of the general problem of scattering by a central field is reduced to a solution of the differential equations (5), and in order to construct $f(\vec{v}\cdot\vec{n})$ it is necessary to know only η_ℓ, the phases of radial functions ψ_ℓ. Finally, a complete effective cross-section of scattering is determined by the formula

$$\sigma = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \eta_\ell. \tag{7}$$

In the case of slow collisions the phases η_ℓ decrease /21 rapidly with an increase of ℓ and, therefore, in formulae (4) and (7) only several of the first terms of the sum are essential. In the case of the slowest collisions (on the order of one electron volt), when the de Broglie wave length is larger than the radius of action of the forces, it is possible to disregard all phases except the zero phase and the problem is reduced to a solution of one common differential equation.

We will formulate the variational principle for such a one dimensional problem. It is necessary to solve the following equation.

$$\left[\frac{d^2}{dr^2} + k^2 - V(r)\right] \psi_0(r) = 0, \tag{8}$$

The condition

$$\psi_0(0) = 0. \tag{9}$$

Then

$$\psi_0(r) \sim A \sin(kr + \eta_0), \tag{10}$$

and the phase of the wave function η_0 is the desired value which determines the effective cross-section. As far as V (r) is concerned, it is sufficient to make the assumption that the function r^2V is finite and is continuous in the interval $0 \leq r < \infty$.

If one should attempt to form a functional, $\int \phi^* H\phi \, d\tau$, that is, in the given case

$$\int_0^\infty \phi^* \left(\frac{d^2}{dr^2} - V\right) \phi dr, \tag{11}$$

analogously to the method used for combined states, we will find that this functional diverges for the function ϕ, which satisfies the conditions of equations (9) and (10), since the behavior of the sub-integral expression at infinity, is as $A^2k^2\sin^2(kr + \eta_0)$. In order to make the functional converge, Hulthen has proposed to add within the brackets under the integral k^2 an expression of the type

$$\int \phi^* (H - E) \phi d\tau. \tag{12}$$

In our case /22

$$I(\phi) = \int \phi(r) \left[\frac{d^2}{dr^2} + k^2 - V(r)\right] \phi(r) \, dr. \tag{13}$$

The functional and its first derivative converge for the function ϕ = a constant, and satisfies the conditions

$$\phi(0) = 0, \ \phi(r) \sim A \sin(kr + \eta), \tag{14}$$

where η is not necessarily the accurate phase η_0. In addition, it is necessary that the sub-integral expression (13) should decrease at infinity faster than 1/r. This places a condition on the consecutive terms of the asymptotic solution of ϕ (r). If we should substitute in this functional the accurate function ψ_0, then it is obvious that this functional would converge to zero.

We will variate the function φ; therefore, we will assume its asymptotic form also changes:

$$\tilde{\varphi} = \varphi + \delta\varphi \sim (A + \delta A) \sin (kr + \eta + \delta\eta); \; \tilde{\varphi}(0) = 0. \tag{15}$$

We will now calculate the variation of the functional I

$$\delta I = \int_0^\infty \delta\varphi \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi \, dr + \int_0^\infty \varphi \left(\frac{d^2}{dr^2} + k^2 - V\right)\delta\varphi \, dr =$$

$$= 2\int_0^\infty \delta\varphi \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi \, dr + (\varphi\delta\varphi' - \varphi'\delta\varphi)\Big|_{r=0}^{r=\infty} \tag{16}$$

The extra integral term can easily be calculated if we utilize (14) and (15)

$$(\varphi\delta\varphi' - \varphi'\delta\varphi)\Big|_{r=0}^{r=\infty} = (\varphi\tilde{\varphi}' - \varphi'\tilde{\varphi})\Big|_{r=0}^{r=\infty} =$$

$$= A(A + \delta A)\, k\, [\sin (kr + \eta) \cos (kr + \eta + \delta\eta) -$$

$$- \cos (kr + \eta) \sin (kr + \eta + \delta\eta)] =$$

$$= - A(A + \delta A)\, k \sin \delta\eta \approx - A^2 k \delta\eta. \tag{17}$$

Thus, if the function φ equals ψ_0, [i.e., it satisfies equation (8) with the conditions of (9) and (10)], then by variating the function ψ_0, we obtain for the functional I (Ref. 11): /23

$$\delta I(\psi_0) = - A^2 k \delta\eta. \tag{18}$$

Consequentially, I (ψ_0) is stationary in relation to any variation which preserves the phase η_0 of the asymptotic solution of ψ_0. The converse is also true; if for a certain function $\varnothing$, the functional I ($\varnothing$) is stationary in relation to an arbitrary variation, which preserves the phase η, then $\varnothing$ satisfies the equation (8). This follows directly from the formulae (16) and (17).

The variational principle can be formulated somewhat differently if we form the functional

$$J(\varnothing) = A^2 k\eta + I(\varnothing). \tag{19}$$

For an accurate wave function, this functional equals $A^2 k'\eta_0$, where this functional is already stationary in relation to the arbitrary variation ψ_0, which preserves the amplitude A. Otherwise

$$A^2 k\eta_0 = \text{stat. val. } \{A^2 k\eta + I(\varnothing)\} = \text{St } \{I(\varnothing)\}. \tag{20}$$

In such a form there appears distinctly an analogy between the phase and the specific value of the discrete spectrum, in which case it is also possible to write

$$E_i = \text{St} \int \varnothing^* H\varnothing d\tau = \text{St } \{\bar{E}\}, \tag{21}$$

with the additional normalization condition $\int \varnothing^* \varnothing \, d\tau = 1$.

There is, however, an essential difference. From the variational principle for a discrete spectrum follow not only stationary but also extreme properties of the functional $\bar{E}$ (by additional conditions of orthogonality). Because of this fact, the actual proper value of the operator H is always less than the value $\bar{E}$; thus, the lower $\bar{E}$, that is the closer $\bar{E}$ is to the actual proper value, the more accurate, generally speaking, is the approximate function which is substituted in the functional. We are concerned here only with the stationarity of J. Consequently, even a roughly approximate function $\varnothing$ might yield an /24 accurate phase value when stated in J ($\varnothing$). We are not able to determine which of these two approximate functions is more accurate, using only this definition.

It is proposed in formula (18) that $\delta A = 0$ and that, consequently, A does not depend on η. Assuming that the standard coefficient A depends in a determined manner on η, thus limiting the number of possible variations, we will come to other useful formulations. For instance, assuming that $A = \frac{1}{\cos \eta}$, we obtain the Kohn formulation (Ref. 16)

$$\delta I = - \frac{k}{\cos^2 \eta_0} \delta \eta_0 = - k \delta (\operatorname{tg} \eta_0). \tag{22}$$

The stationary expression for $\operatorname{tg} \eta_0$ may be stated as follows:

$$k \operatorname{tg} \eta_0 = St \{J_1 (\varphi)\} = St \{k \operatorname{tg} \eta + I (\varphi)\} \tag{23}$$

whereby it is assumed that the asymptotic behavior of the function φ is determined by the formula

$$\varphi \sim \frac{1}{\cos \eta} \sin (kr + \eta) = \sin kr + \operatorname{tg} \eta \cos kr. \tag{24}$$

If we assume that $A = \frac{1}{\sin \eta}$, then we will obtain a stationary expression for $\operatorname{ctg} \eta_0$

$$- k \operatorname{ctg} \eta_0 = St \{J_2\} = St \{- k \operatorname{ctg} \eta + I\}; \tag{25}$$

where

$$\varphi \sim \operatorname{ctg} \eta \cdot \sin kr + \cos kr. \tag{26}$$

Both these methods of standardization are inconvenient because in certain cases the multiplier A and the functionals J_1 and J_2 are transformed into infinity. More convenient in this relation is the standardization $A = 1$. Then

$$\eta_0 = St \left\{\eta + \frac{1}{k} \int_0^\infty \varphi \left(\frac{d^2}{dr^2} + k^2 - V\right) \varphi \, dr\right\}. \tag{27}$$

Generally, the stationary expression for a certain function /25
of the phase $f(\eta_0)$ will be obtained if we put $A = \sqrt{f'(\eta)}$. Then

$$f(\eta_0) = \mathrm{St}\left\{f(\eta) + \frac{1}{k}\int_0^\infty \varphi\left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi\, dr\right\}, \tag{28}$$

and

$$\varphi(r) \sim \sqrt{f'(\eta)}\,\sin(kr + \eta).$$

We have developed here a variational principle for the case $\ell = 0$, that is, for the so-called s-scattering. However, it is completely clear that the case $\ell \neq 0$ will differ only by the addition of the term $\ell(\ell+1)/r^2$ to the potential V in all formulae and the constant phase $\frac{\ell\pi}{2}$ in the asymptotic form of the function. These additions will have no effect on the calculations, and the formulation of the variational principle will remain the same:

$$\left.\begin{aligned}
\delta I(\psi_\ell) &= \delta\int_0^\infty \psi_\ell\left(\frac{d^2}{dr^2} + k^2 - V - \frac{\ell(\ell+1)}{r^2}\right)\psi_\ell\, dr = \\
&= -k\delta\eta_\ell, \\
\eta_\ell &= \mathrm{St}\left\{\eta + \frac{1}{k}\int_0^\infty \varphi\left(\frac{d^2}{dr^2} + k^2 - V - \frac{\ell(\ell+1)}{r^2}\right)\varphi\, dr\right\};
\end{aligned}\right\} \tag{29}$$

$$\left.\begin{aligned}
&\psi_\ell(0) = 0,\ \psi_\ell \sim \sin\left(kr - \frac{\ell\pi}{2} + \eta_\ell\right), \\
&\varphi(0) = 0,\ \varphi \sim \sin\left(kr - \frac{\ell\pi}{2} + \eta\right).
\end{aligned}\right\} \tag{30}$$

§5. The Variational Principle For A Potential Which Has A Coulomb Character at Infinity

We have investigated, until now, the potentials which decrease at large r no slower than at $1/r^2$. However, during collisions of electrons with ions, the field decreases, for instance, as $1/r$ and this case is /26 always essential.

Since the field is spherically symmetrical, it is possible (as before) to resolve $\Psi(r)$ by spherical functions and thus we arrive, as previously, at the equation

$$\left[\frac{d^2}{dr^2} + k^2 - V(r)\right] \psi(r) = 0, \tag{1}$$

where V (r) has the form of

$$V(r) = \frac{c}{r} + v(r), \tag{2}$$

and V (r) decreases no slower than $1/r^2$. We form the functional

$$I = \int_0^\infty \varphi \left[\frac{d^2}{dr^2} + k^2 - \frac{c}{r} - v(r)\right] \varphi(r)\, dr. \tag{3}$$

If we substitute in this functional the function φ with the common asymptotic behavior $\varphi \sim \sin(kr + \eta)$, then it is expedient that the term which contains c/r will yield a divergent expression during the integration. The asymptotic coulomb character of the field changes the behavior of the wave functions. We should state as known quantities

$$\varphi \sim \sin(kr + \eta + \alpha \ln kr), \tag{4}$$

and pick α to eliminate the divergent term of infinity. We have

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{c}{r} - v(r)\right] \sin(kr + \alpha \ln kr + \eta) =$$

$$= -\frac{2k\alpha + c}{r} \sin(kr + \alpha \ln kr + \eta) + 0(1/r^2). \quad (5)$$

It can be seen from this that $2k\alpha = -c$ and, consequently

$$\varphi \sim \sin\left(kr - \frac{c}{2k} \ln kr + \eta\right). \quad (6)$$

In the integral we will variate the accurate solution of the equation /27 assuming that

$$\tilde{\psi} = \psi + \delta\psi \sim A \sin\left(kr - \frac{c}{2k} \ln kr + \eta + \delta\eta\right);$$

$$\tilde{\psi}(0) = 0. \quad (7)$$

We will obtain

$$I(\tilde{\psi}) = I(\psi) + \delta I = \delta I = (\psi\delta\psi' - \psi'\delta\psi)\Big|_{r=0}^{r=\infty} =$$

$$= -\left[A^2\left(k - \frac{c}{2kr}\right)\sin\delta\eta\right]_{r\to\infty} = -A^2k\delta\eta. \quad (8)$$

Thus, we will obtain formally the same results as we did in the first case; however, here the sense of the phase η is entirely different. The formulation of the phase method for the potential which has a coulomb character at infinity is present, for instance, in the book by Landau and Lifshitz (Ref. 36, Section 106); $f(\theta)$ is determined as before by the phases η_l, but with a more complicated method. The complete effective cross-section σ, as is known, diverges in the case of the field which has a coulomb character at infinity.

§6. The General Problem of Elastic Scattering of Particles And The Variational Principle By Kohn

We will examine the case when the scattering center does not have, generally speaking, a spherical symmetry. Then the problem is to deduce a solution of the equation

$$(\nabla^2 + k^2 - V)\ \Psi\ (\vec{r}) = 0. \tag{1}$$

The character of interaction of particles with the scatterer is determined by the operator V. In a simpler case this is simply a material function of the coordinates $V(\vec{r})$; that is, the dispersion takes place under the influence of potential forces which depend only on the position of the particle. It is possible to assume that the function $V(\vec{r})$ is complex, then the operator V is self-conjugate and during the processes of scattering the particles will either be absorbed or eliminated. The full current which will pass through a large radius sphere will, generally /28 speaking, equal zero. In a more general case, it might be considered that V is a certain integral operator.

$$V\Psi\ (\vec{r}) = \int K\ (\vec{r}, \vec{r}')\ \Psi\ (\vec{r}')\ d\tau', \tag{2}$$

and the properties of the operator V are determined by the properties of the nucleus K.

Considering that the process of scattering is characterized by equation (1), our main assumption is contained in the fact that particles with a given energy might be scattered, absorbed and created, but cannot change their energy; that is the frequency of the incident wave and the frequency of the scattered wave are identical. Thus, we have eliminated from our investigation all inelastic processes. By introducing the anti-conjugate addition to the operator we are able, for instance, to consider that the amount of elastic scattering of particles will be less than the amount of incident particles; however, such a consideration will be purely phenomenological.* For a detailed investigation of inelastic processes, a dynamic examination of this scattering center itself is necessary.

In order to formulate a variational principle we should investigate together with a solution to equation (1), which has a common asymptotic form

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*They are primarily received in this way: for example in the description of the elastic scattering of neutrons by the nuclei.

$$\Psi(\vec{v}, \vec{r}) \sim e^{ik\vec{v}\cdot\vec{r}} + f(\vec{v}, \vec{n}) \frac{e^{ikr}}{kr}, \quad (3)$$

also the solution to a hermitian conjugate equation

$$(\nabla^2 + k^2 - V^+) \Phi = 0, \quad (4)$$

which will contain, in the case of large r

$$\Phi(\vec{v}, \vec{n}) \sim e^{ik\vec{v}\cdot\vec{r}} + f(\vec{v}, \vec{n}) \frac{e^{-ikr}}{kr}, \quad (5)$$

in addition to the incident wave, only convergent waves will thus satisfy the "reverse" emission principle. It is obvious that the scattering process can be characterized only by the function Φ^* which, after the substitution of $\vec{v}$ by $-\vec{v}$, takes on a common asymptotic form (3) and /29 is the solution to the equation

$$(\nabla^2 + k^2 - V^{+*}) \Phi^*(-\vec{v}, \vec{r}) =$$

$$= (\nabla^2 + k^2 - V') \Psi'(\vec{v}, \vec{r}) = 0. \quad (6)$$

In this case V' signifies the transpose operator; the nucleus K' is related to the nucleus of the operator V by the formula

$$K'(\vec{r}, \vec{r}') = K(\vec{r}', \vec{r}). \quad (7)$$

If the operator V, in particular, is a functional, (diagonal in a coordinate presentation) then V = V' and

$$\Psi(\vec{v}, \vec{r}) = \Psi'(\vec{v}, \vec{r}).$$

We will construct the functional

$$I = \int \Phi^*(\vec{v}_2, \vec{r}) (\nabla^2 + k^2 - V) \Psi(\vec{v}_1, \vec{r}) d\tau =$$

$$= \int \Psi'(-\vec{v}_2, \vec{r}) (\nabla^2 + k^2 - V) \Psi(\vec{v}_1, \vec{r}) d\tau, \quad (8)$$

which obviously converts into zero for the accurate functions Φ and Ψ. We will search for the variation of this functional, assuming that the asymptotic form of the variated functions is also subjected to a change.

$$\tilde{\Psi}(\vec{v}_1, \vec{r}) = \Psi_1 + \delta\Psi_1 \sim$$

$$\sim e^{ik\vec{v}_1\cdot\vec{r}} + [f(\vec{v}_1, \vec{n}) + \delta f(\vec{v}_1, \vec{n})]\frac{e^{ikr}}{kr}; \quad (9)$$

$$\tilde{\Psi}'(\vec{v}_2, \vec{r}) = \Psi_2 + \delta\Psi_2 \sim$$

$$\sim e^{ik\vec{v}_2\cdot\vec{r}} + [f'(\vec{v}_2, \vec{n}) + \delta f'(\vec{v}_2, \vec{n})]\frac{e^{ikr}}{kr}. \quad (10)$$

Then, by dropping the second order magnitude

$$\int \delta\Psi_2' (\nabla^2 + k^2 - V)\, \delta\Psi_1 \, d\tau,$$

we obtain

$$\delta I = \int \Psi_2' (\nabla^2 + k^2 - V)\, \delta\Psi_1 \, d\tau.$$

Obviously, the variation of the function Ψ_2' does not change the functional in this approximation.

We will divide all space into two parts by the spherical radius R with its center at the origin of the coordinates and we will utilize /30 Green's formula. Then

$$\delta I = \int_{S_R} \left(\Psi_2' \frac{\partial}{\partial r}\delta\Psi_1 - \delta\Psi_1 \frac{\partial}{\partial r}\Psi_2'\right)_{r=R} dS +$$

$$+ \int_{r<R} \delta\Psi_1 (\nabla^2 + k^2 - V')\, \Psi_2' \, d\tau +$$

$$+ \int_{r>R} \Psi_2' (\nabla^2 + k^2 - V)\, \delta\Psi_1 \, d\tau. \quad (12)$$

The second integral in the right part exactly equals zero, and the third integral approaches zero as $R \to \infty$. During the search for the limit of the first integral we may substitute, instead of the function $\delta\Psi_1$ and Ψ_2, their asymptotic form and then drop all terms appearing under the integral, which decrease more rapidly than R^{-2}, since when $R \to \infty$ the integral of these terms will approach zero along the surface of the sphere. The integral of the terms which decreases just like R^{-2}, but contain the flat wave will also tend towards zero, due to the presence of an oscillating multiplier $e^{ikR\vec{v}\cdot\vec{n}}$. Thus, we have

$$\delta I = \lim_{R\to\infty} \int_{S_R} \left\{\left[e^{-ik\vec{v}_2\cdot\vec{r}} + f'(-\vec{v}_2, \vec{n})\frac{e^{ikr}}{kr}\right]\frac{\partial}{\partial r}\left[\delta f(\vec{v}_1, \vec{n})\frac{e^{ikr}}{kr}\right]\right.$$

$$\left. - \left[\delta f(\vec{v}_1, \vec{n})\frac{e^{ikr}}{kr}\right]\frac{\partial}{\partial r}\left[e^{-ik\vec{v}_2\cdot\vec{r}} + f'(-\vec{v}_2, \vec{n})\frac{e^{ikr}}{kr}\right]\right\}_{r=R} dS =$$

$$= \lim_{R\to\infty} \int \left[e^{-ik\vec{v}_2\cdot\vec{r}}\frac{e^{ikr}}{kr}\cdot ik - \frac{e^{ikr}}{kr}e^{-ik\vec{v}_2\cdot\vec{r}}(-ik\vec{v}_2\cdot\vec{n})\right]_{r=R} x$$

$$x\,\delta f(\vec{v}_1, \vec{n})\,dS = \lim_{R\to\infty} iR\int_0^{2\pi} d\varphi \int_0^{\pi} e^{ikR(1-\cos\theta)}(1+\cos\theta)\,x$$

$$x\,\delta f\cdot\sin\theta\cdot d\theta = \lim_{R\to\infty} iR\int_0^{2\pi} d\varphi \int_0^{2} e^{ikR\gamma}(2-\gamma)\,\delta f\cdot d\gamma. \qquad (13)$$

In this case the direction $\vec{v}_2$, as a polar axis within the spherical coordinates, was selected. During the differentiation of r, the term which is proportional to R^{-2} was dropped and the exchange of $1 - \cos\theta = \gamma$ was conducted. We will partially integrate the integral by γ. Then /31

$$\delta I = \lim_{R\to\infty}\int_0^{2\pi} d\varphi \left\{\left[\frac{1}{k}e^{ikR\gamma}(2-\gamma)\,\delta f\right]\Big|_{\gamma=0}^{\gamma=2} - \right.$$

$$\left. - \frac{1}{k}\int_0^2 e^{ikR\gamma}\frac{\partial}{\partial\gamma}[(2-\gamma)\,\delta f]\,d\gamma\right\}. \qquad (14)$$

The internal integral in this formula tends toward 0 when $R \to \infty$; the extra integral term converts into 0 on the upper limit, and on the lower limit it equals

$$\left[\frac{1}{k} e^{ikR\gamma} (2 - \gamma)\ \delta f\right]_{\gamma=0} = \left[\frac{2}{k}\ \delta f\right]_{\theta=0} = \frac{2}{k}\ \delta f\ (\vec{v}_1, \vec{v}_2). \qquad (15)$$

It is obvious that when $\theta = 0$ the function δf does not depend on $\varnothing$, and we finally obtain

$$\delta I = \delta \int \Psi'\ (-\vec{v}_2, \vec{r})\ (\nabla^2 + k^2 - V)\ \Psi\ (\vec{v}_1, \vec{r})\ d\tau =$$

$$= -\frac{4\pi}{k}\ \delta f\ (\vec{v}_1, \vec{v}_2). \qquad (16)$$

This same formula can be acquired somewhat differently by resolving expressions (9) and (10) by the spherical functions for the asymptotic form of the function Ψ_1 and Ψ_2' and by substituting the proper solutions in formula (12). This method is used for the solution of analogous formulas in Chapter III.

We will now examine a general bilineal functional

$$I\ (\varnothing_2, \varnothing_1) = \int \varnothing_2\ (\nabla^2 + k^2 - V)\ \varnothing_1\ d\tau, \qquad (17)$$

where $\varnothing_1$ and $\varnothing_2$ are arbitrary functions which have the following asymptotic form

$$\varnothing_i \sim e^{ik\vec{v}_i \cdot \vec{r}} + g_i\ (\vec{n})\ \frac{e^{ikr}}{kr} \qquad (i = 1,2). \qquad (18)$$

Then, on the basis of (16), it is possible to confirm that if the variation $\delta\varnothing_1$ and $\delta\varnothing_2$ change only the amplitude $g_i(\vec{n})$ in formula (18) then the functional /32

$$J = g_1\ (-\vec{v}_2) + \frac{k}{4\pi}\ I\ (\varnothing_2, \varnothing_1), \qquad (19)$$

is stationary in relation to all these variations only in the case if $\Phi_2 = \Psi' (\vec{v}_2, r)$, $\Phi_1 = \Psi (\vec{v}_1, \vec{r})$. In that case the functional J itself will be equal to the amplitude of scattering $f (\vec{v}_1, -\vec{v}_2)$. Thus,

$$f (\vec{v}_1, -\vec{v}_2) = St \left\{ J (\Phi_2, \Phi_1) \right\}. \qquad (20)$$

If the operator V is symmetrical, then the function $\Psi' (\vec{v}_2, \vec{r}) = \Psi(\vec{v}_2, \vec{r})$ is the solution to that same equation (1) and during the examination of the variational principle we deal only with one problem of scattering: the problem which is characterized by equation (1).
If the conditions of symmetry are not observed, then we should investigate two problems: in one of these problems the interaction with the scatterer is characterized by the operator V and in the other problem - by the operator V'. Particularly if the operator V is self-conjugated (hermitian), then V' = V* and the second problem is characterized by the complex hermitian operator V*. Such a problem occurs for instance if we consider the magnetic interaction between the bombarding particle and the scatterer; the operator is then complex and self-conjugated.

The wave functions $\Psi (\vec{v}, \vec{r})$, $\Phi (\vec{v}, \vec{r})$, which we are investigating here, have the form of a flat wave $e^{ik\vec{v}\cdot\vec{r}}$ at infinity and, thus, characterize the state of a free particle in the presence of large r with a determined impulse $k\vec{v}$. The scattering amplitude $f (\vec{v}_1, \vec{v}_2)$ determines the proper validity of transition of this particle from a state with an impulse $k\vec{v}_1$ into a state with impulse $k\vec{v}_2$ as a result of scattering.

Returning to the common hermitian definition of the functional I

$$I = \int \Phi_2^* (\nabla^2 + k^2 - V) \Psi_1 \, d\tau, \qquad (21)$$

We are able to formulate the results of this section in a general form. /33

Let us examine the transition from a certain original state I into the final state II, the probability of which is determined by the square of the coefficient of the scattering amplitude f. Let us further assume that the functions Ψ_1 and Φ_2, when substituted in the functional I (invariated as well as variated), satisfy the conditions:

1. a) The fundamental term of the asymptotic solution of the function Ψ_1 (which does not disappear when $r \to \infty$) characterizes the original state of the particle I;
   b) the fundamental term of the asymptotic solution to the function Ψ_2 characterizes the final state of the particle II.

2. a) In addition to the fundamental term the asymptotic solution to the function Ψ_1 (among the terms which decrease as r^{-1}) contains divergent waves only; that is, Ψ_1 satisfies the direct principle of emission.
   b) In addition to the principal term, the asymptotic solution to the function Φ_2 contains convergent waves only; that is, Φ_2 satisfies the reverse principle of emission.

If, in addition, the following conditions were carried out,

3. a) The function Ψ_1 is the solution to equation (1) which characterizes scattering,
   b) The function Φ_2 is the solution to conjugated equation (4),

then the variation of the functional I is proportional to the variation of the corresponding amplitude of scattering f in the function Ψ_1.

The reverse assertion which can be formulated as follows is also justified:

If in the case of not variated and variated functions conditions 1 and 2 were carried out; if in addition, in the case of arbitrary variations $\delta\Psi_1$ and $\delta\Phi_2$ which decrease at infinity more rapidly than r^{-2}, the variational functional I equals 0, then condition 3 is fulfilled.

After proper corrections this formulation of the variational principle proves to be accurate in the case of more general problems in collision theory.

§7. Elastic Scattering of Electrons By A Complex Atom And Calculation of Exchange

/34

The variational principle which was formulated in the preceding section may be generalized in the case of a collision between electrons and atoms. For the sake of simplicity and concreteness we will, henceforth, consider collisions between electrons and atoms of hydrogen;

however, after obvious generalizations the results will also be applicable for more complicated problems.

The Schroedinger equation in a given case will have the following form

$$L\Psi = \left(\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} - \right.$$

$$\left. - \frac{2}{r_{12}} + k^2 - 1 \right) \Psi (\vec{r}_1, \vec{r}_2) = 0, \qquad (1)$$

$$E = \frac{1}{2} (k^2 - 1).$$

The complete energy E consists of the energy of the bombarding electron $\frac{k^2}{2}$ and the energy of the hydrogen atom in the fundamental state $E_0 = -\frac{1}{2}$.

We will assume in this section that the energy of the bombarding electrons is not sufficient to excite the atom; that is

$$\frac{k^2}{2} < E_0 - E_1 = \frac{1}{2} - \frac{1}{8} = \frac{3}{8} . \qquad (2)$$

Then the wave function will have the following asymptotic form

$$(\vec{v}, \vec{r}_1, \vec{r}_2) \sim \begin{cases} \psi_0 (r_1) \left[e^{ik\vec{v}\cdot\vec{r}_2} + f (\vec{v}, \vec{n}_2) \frac{e^{ikr_2}}{kr_2} \right], & r_2 \to \infty \\ \psi_0 (r_2) \, g (\vec{v}, \vec{n}_1) \frac{e^{ikr_1}}{kr_1} , & r_1 \to \infty \end{cases} \qquad (3)$$

whereby the wave function of the fundamental state of hydrogen /35
$\psi_0 = \frac{1}{\sqrt{\pi}} e^{-r}$ satisfies the equation

$$\left(\nabla^2 + \frac{2}{r} - 1\right) \psi_0 (r) = 0, \qquad (4)$$

as well as the condition of standardization and is a material function.

The scattering amplitude f ($\vec{v}_1$ and $\vec{v}_2$) characterizes the elastic scattering and g ($\vec{v}_1$ and $\vec{v}_2$) characterizes scattering with an exchange. As a result of the similarity of electrons, these processes are distinguishable only if the spins of both electrons are antiparallel. In that case the effective cross-section equals

$$\sigma_1 = \frac{1}{k^2}\left(|f|^2 + |g|^2\right). \tag{5}$$

If, on the other hand, the spins of the bombarding and atomic electrons are parallel, then the coordinate function should be antisymmetric and we obtain for the effective cross-section

$$\sigma_2 = \frac{1}{k^2}|f - g|^2. \tag{6}$$

By neutralizing all possible orientations of the spins of the bombarding and atomic electrons, we obtain two cases of parallel and two cases of antiparallel orientations. Thus

$$\sigma = \frac{1}{2}\sigma_1 + \frac{1}{2}\sigma_2 = \frac{1}{k^2}\left(\frac{1}{2}|f|^2 + \frac{1}{2}|g|^2 + \frac{1}{2}|f - g|^2\right) =$$

$$= \frac{1}{k^2}\left(|f|^2 + |g|^2 - \frac{1}{2}fg^* - \frac{1}{2}f^* g\right) =$$

$$= \frac{1}{k^2}\left(\frac{1}{4}|f + g|^2 + \frac{3}{4}|f - g|^2\right) = \frac{1}{4}\sigma^+ + \frac{3}{4}\sigma^-. \tag{7}$$

We can see from this that, during the calculation of the effective cross-section for a two-electron problem, it is possible to search first for the coordinate of the wave function Ψ with an asymptotic form (3); this, without taking into consideration the Pauli principle and the symmetry properties, should be considered only during the calculation of their effective cross-section by known amplitudes f and g. It is possible, /36 however, to consider the properties of symmetry from the very beginning and to look for a solution to equation (1) $\Psi^{\pm}$, which satisfies the condition

$$\Psi^{\pm}(\vec{r}_1, \vec{r}_2) = \pm \Psi^{\pm}(\vec{r}_2, \vec{r}_1) \tag{8}$$

and which has the following asymptotic form

$$\Psi^{\pm} \sim \begin{cases} \frac{1}{\sqrt{2}} \psi_0 (r_1) \left[e^{ik\vec{v}\cdot\vec{r}_2} + f^{\pm}(\vec{v}, \vec{n}_2) \frac{e^{ikr_2}}{kr_2} \right], & r_2 \to \infty , \\ \pm \frac{1}{\sqrt{2}} \psi_0 (r_2) \left[e^{ik\vec{v}\cdot\vec{r}_1} + f^{\pm} (\vec{v}, \vec{n}_1) \frac{e^{ikr_1}}{kr_1} \right], & r_1 \to \infty . \end{cases} \tag{9}$$

A symmetric function corresponds to the full spin S = 0, the antisymmetric function corresponds to the spin S = 1. The effective cross-section which was neutralized by the directions of the spins is then calculated by the formula

$$\sigma = \frac{1}{4} \sigma^{+} + \frac{3}{4} \sigma^{-} = \frac{1}{k^2} \left(\frac{1}{4} |f^{+}|^2 + \frac{3}{4} |f^{-}|^2 \right). \tag{10}$$

It is obvious that the functions $\Psi^{\pm}$ can easily be obtained from the function Ψ;

$$\Psi^{\pm} (\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi (\vec{r}_1, \vec{r}_2) \pm \Psi (\vec{r}_2, \vec{r}_1)] . \tag{11}$$

We will now examine the functional

$$(\varphi_2, \varphi_1) = \iint \varphi_2 L \varphi_1 \, d\tau_1 \, d\tau_2 , \tag{12}$$

whereby the asymptotic form of the function φ_1, φ_2 is analogous to the asymptotic form of the function Ψ

$$\varphi_i \sim \begin{cases} \psi_0 (\vec{r}_1) \left[e^{ik\vec{v}\cdot\vec{r}_2} + F_i (\vec{n}_2) \frac{e^{ikr_2}}{kr_2} \right], & r_2 \to \infty , \\ \psi_0 (\vec{r}_2) \, G_i (\vec{n}_1) \frac{e^{ikr_1}}{kr_1} , & r_1 \to \infty . \end{cases} \tag{13}$$

$$(i = 1,2)$$

where F_i, G_i are certain arbitrary functions of the direction of the unit vector $\vec{n}$. First, it is necessary to convince oneself that the integral I is convergent. For this purpose it is necessary to investigate the /37 behavior of the desired integral expression for large r_1 and large r_2. Utilizing the asymptotic form of the function φ (13), we obtain in the case of large r_2

$$L\varphi_i \sim (\nabla_1^2 + \nabla_2^2 +$$

$$+ \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}} + k^2 - 1)\ \psi_0(\vec{r}_1)\left(e^{ik\vec{v}_1\cdot\vec{r}_2} + F_1\frac{e^{ikr_2}}{kr_2}\right) =$$

$$= \psi_0(r_1)\left[\left(\frac{2}{r_2} - \frac{2}{r_{12}}\right)\left(e^{ik\vec{v}_1\cdot\vec{r}_2} + F_1\frac{e^{ikr_2}}{kr_2}\right) + 0\left(\frac{1}{r_2^3}\right)\right]. \qquad (14)$$

The terms on the order of r_2^{-3} are obtained during the effects of the angular part of the Laplace operator on the function F and also, possibly, from the consecutive terms in the asymptotic solution φ_1. Thus, the terms which are essential and the sub-integral expression have the following form:

$$\psi_0^2(r_1)\left(\frac{2}{r_2} - \frac{2}{r_{12}}\right)\left(e^{ik\vec{v}_2\cdot\vec{r}_2} + F_2\frac{e^{ikr_2}}{kr_2}\right)\left(e^{ik\vec{v}_1\cdot\vec{r}_2} + F_1\frac{e^{ikr_2}}{kr_2}\right). \qquad (15)$$

If we should integrate in the beginning with respect to $\vec{r}_1$, then we come to the calculation of the integral

$$\int \psi_0^2(r_1)\left(\frac{2}{r_2} - \frac{2}{r_{12}}\right)d\tau_1, \qquad (16)$$

which can be considered as a potential neutral system consisting of a change which is located at the origin of the coordinates and a change of the opposite symbol which is distributed with a density $\psi_0^2(r_1)$. In our case, the integral (16) decreases exponentially and, consequently, the convergence of the integral at large r_2 is assured. Similar reasoning might also be applied in the case of large r_1.

However, this entire reasoning is true only in the case of electron scattering by a neutral atom. In the case of a scattering of an ion the integral (16) will decrease only as r_2^{-1}, since the central and distributed charges will not compensate completely. In that case it is necessary to complicate the asymptotic form of the function φ_i in a manner analogous to that used in Section 5.

We will now examine the variation of the functional I, substituting in it $\varphi_1 = \Psi_1$, $\varphi_2 = \Psi_2$ [the correct solutions to equation (1) with an asymptotic form (3)]. Thereby, in the case of Ψ_1, we will have $\vec{v} = \vec{v}_1$; in the case of Ψ_2 we will have $\vec{v} = \vec{v}_2$. In a given case the interaction of the electron with the scatterer will be characterized by the material and self-conjugated operator; therefore, the functions Ψ_1 and Ψ_2 should be the solutions to equation (1), alone. First, we will assume that during the variation of the functions Ψ_1, Ψ_2 in the asymptotic form, only the scattering amplitudes are subjected to a change. /38

$$\tilde{\Psi}_i = \Psi_i + \delta\Psi_i \sim \begin{cases} \psi_0(r_1)\left[e^{ik\vec{v}_i\cdot\vec{r}_2} + \right. \\ \left. + \left(f(\vec{v}_i, \vec{n}_2) + \delta_i f\right)\frac{e^{ikr_2}}{kr_2}\right], \quad r_2 \to \infty, \\ \psi_0(r_2)\left(g(\vec{v}_i, \vec{n}_1) + \delta_i g\right)\frac{e^{ikr_1}}{kr_1}, \quad r_1 \to \infty. \end{cases} \tag{17}$$

Then

$$\delta I = \iint \Psi_2 L\delta\Psi_1 \, d\tau_1 \, d\tau_2 = \lim_{\substack{R_1 \to \infty \\ R_2 \to \infty}} \int_{r_1 \leq R_1} d\tau_1 \int_{r_2 \leq R_2} \Psi_2 L\delta\Psi_1 \, d\tau_2 =$$

$$= \lim_{\substack{R_1 \to \infty \\ R_2 \to \infty}} \left[\int_{r_1 \leq R_1} d\tau_1 \int_{r_2 \leq R_2} \delta\Psi_1 L\Psi_2 \, d\tau_2 + \right.$$

$$+ \int_{r_2 \leqslant R_2} d\tau_2 \int_{r_1 = R_1} \left(\Psi_2 \frac{\partial}{\partial r_1} \delta\Psi_1 - \delta\Psi_1 \frac{\partial}{\partial r_1} \Psi_2 \right) dS_1 +$$

$$+ \int_{r_1 \leqslant R_1} d\tau_1 \int_{r_2 = R_2} \left(\Psi_2 \frac{\partial}{\partial r_2} \delta\Psi_1 - \delta\Psi_1 \frac{\partial}{\partial r_2} \Psi_2 \right) dS_2 \Big]. \qquad (18)$$

The first integral equals 0 since Ψ_2 satisfies equation (1). In the second and third integrals we can substitute instead of Ψ_2 and $\delta\Psi_1$ their asymptotic expressions. Then, the integration, with respect to the volume and surface, can be made independently and the volumetric integral of Ψ_0^2 tends within its limits toward unity. In the case of large values r_1 the functions Ψ_2 and $\delta\Psi_1$ contain only the divergent waves and, accordingly, the surface integral by dS_1 will also become zero. The integral by dS_2 does not differ at all from the integral (6.13), which was calculated in the preceding section. Thus, we obtain /39

$$\delta I \left[\Psi_2 (\vec{r}_1, \vec{r}_2), \Psi_1 (\vec{r}_1, \vec{r}_2) \right] = - \frac{4\pi}{k} \delta f (\vec{v}_1, - \vec{v}_2). \qquad (19)$$

If, instead of the function $\Psi_2 (\vec{r}_1, \vec{r}_2)$, we would substitute in the functional the function $\Psi_2 (\vec{r}_2, \vec{r}_1)$, then by repeating the derivative we obtain

$$\delta I \left[\Psi_2 (\vec{r}_2, \vec{r}_1), \Psi_1 (\vec{r}_1, \vec{r}_2) \right] = - \frac{4\pi}{k} \delta g (\vec{v}_1, \vec{v}_2). \qquad (20)$$

If, in the functional I, we would substitute the wave function $\Psi_1^{\pm}$, $\Psi_2^{\pm}$, then by utilizing formula (11), we will obtain

$$\delta I (\Psi_2^{\pm}, \Psi_1^{\pm}) = - \frac{4\pi}{k} \delta f^{\pm} (\vec{v}_1, - \vec{v}_2). \qquad (21)$$

By utilizing formulae (19) - (21) it is possible to construct the functionals J, which give a stationary expression for the amplitudes f and g or the amplitudes $f^{\pm}$, in a manner analogous to that used in Sections 4 and 6 for more simple problems.

However, the variational principles are applicable in practice to a very limited class of problems in this form. Actually, by variating the functions Ψ_1, Ψ_2, we assume that the wave function of the fundamental state of the atom ψ_0 remains unchanged. Consequently, in order to write the function φ_i which we can substitute in a functional I, it is necessary to know precisely the wave function of the fundamental state of the atom. This is possible only for the case of a collision between electrons with the hydrogen atom which was examined here. If, on the other hand, we attempt to substitute in I the function with an approximate wave function $\tilde{\psi}_0 = \psi_0 + \delta\psi_0$, then in the case of large r_1, r_2 the function $L\varphi_1$ will not decrease and the integral will diverge.

This difficulty can be overcome if we assume that, simultaneously with the variation of the function ψ_0, the operator L also variates so that the functional remains convergent. For this purpose it is necessary that the operator contain, instead of $2\bar{E}_0 = -1$ the value $2\bar{E}_0 \int \tilde{\psi}_0 \left(-\nabla^2 - \frac{1}{r}\right)\tilde{\psi}_0 \, d\tau$ which differs for various functions. Such a changed /40 operator L should, therefore, not be considered during the calculation of the first variation I, since from the variational principle for a discrete spectrum we know that the variation $\delta\bar{E} = 0$ under the condition that the standardization of the function $\tilde{\psi}_0$ is preserved. In that case

$$\tilde{\Psi}_i = \Psi_i + \delta\Psi_i \sim \begin{cases} [\psi_0(r_1) + \delta\psi_0]\left[e^{ik\vec{v}_i\cdot\vec{r}_2} + \right. \\ \left. + (f_i + \delta f_i)\frac{e^{ikr_2}}{kr_2}\right], \; r_2 \to \infty, \\ [\psi_0(r_2) + \delta\psi_0](g_i + \delta g_i)\frac{e^{ikr_1}}{kr_1}, \; r_1 \to \infty. \end{cases} \tag{22}$$

It is easy to convince oneself that in formula (18) for δI in the first surface integral, which was already calculated in Section 6, one more term will be added.

$$\lim_{\substack{R_1\to\infty\\ R_2\to\infty}} \int_{r_1\leq R_1} \psi_0(r_1)\,\delta\psi_0(\vec{r}_1)\,d\tau_1 \int_{r_2=R_2} \left[\left(e^{ik\vec{v}_2\cdot\vec{r}_2} + f(\vec{v}_2, \vec{n}_2)\,\frac{e^{ikr_2}}{kr_2}\right) x\right.$$

$$x\,\frac{\partial}{\partial r_2}\left(e^{ik\vec{v}_1\cdot\vec{r}_2} + f(\vec{v}_1, \vec{n}_2)\,\frac{e^{ikr_2}}{kr_2}\right) - \left(e^{ik\vec{v}_1\cdot\vec{r}_2} + f(\vec{v}_1, \vec{n}_2)\,\frac{e^{ikr_2}}{kr_2}\right) x$$

$$\left. x\,\frac{\partial}{\partial r_2}\left(e^{ik\vec{v}_2\cdot\vec{r}_2} + f(\vec{v}_2, \vec{n}_2)\,\frac{e^{ikr_2}}{kr_2}\right)\right] dS_2. \qquad (23)$$

By calculating the surface integral with the method which is analogous to that already applied in Section 6,* we obtain zero and, thus, the external form of the variational principle changes once again.

$$\delta I(\psi_2, \psi_1) = -\frac{4\pi}{k}\,\delta f(\vec{v}_1, -\vec{v}_2). \qquad (24)$$

However, the functional I has already a somewhat different form

$$I(\varphi_2, \varphi_1) = \iint \varphi_2 \left(\nabla_1^2 \quad \frac{2}{2} + \frac{2}{r_1} + \frac{2}{r_2} - \right.$$

$$\left. - \frac{2}{r_{12}} + k^2 + 2E\right) \varphi_1\, d\tau_1\, d\tau_2, \qquad (25)$$

where /41

$$\varphi_i \sim \begin{cases} \varphi(\vec{r}_1)\left(e^{ik\vec{v}_1\cdot\vec{r}_2} + F(\vec{n}_2)\,\frac{e^{ikr_2}}{kr_2}\right), & r_2 \to \infty, \\ \varphi(\vec{r}_2)\,G(\vec{n}_1)\,\frac{e^{ikr_1}}{kr_1}, & r_1 \to \infty; \end{cases} \qquad (26)$$

*This type of integral is examined in more detail in Chapter III.

$\varphi(\vec{r})$ satisfies the condition $\int |\varphi(\vec{r})|^2 d\tau = 1$;

$$\overline{E} = \int \varphi^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r} \right) \varphi \, d\tau, \tag{27}$$

and the variational function is determined by formula (22).

It is also easy to formulate the variational principle in a similar form for an elastic collision of electrons with any given multi-electron atom.

§8. Variational Principle for Inelastic Collisions

In this case we will proceed in accordance with a fundamental idea which was expressed in Section 6; that is, we will examine the variational functional

$$\int \Psi_2 (H - E) \Psi_1 \, d\tau,$$

substituting, instead of Ψ_1, the wave function which corresponds to the original state and, instead of Ψ_2, the wave function which corresponds to the final state. In order to avoid cumbersome definitions we will consider the collisions of electrons with hydrogen atoms, as before.

If we assume that before the collision the atom of hydrogen was, generally speaking, in a certain excited state with the wave function $\psi_i(\vec{r})$, then the corresponding wave function which satisfies equation (7.1) will have the following asymptotic form.

$$\Psi^{(i)}(\vec{v}; \vec{r}_1, \vec{r}_2) \sim \begin{cases} \varphi_i(\vec{r}_1) \, e^{ik_i \vec{v} \cdot \vec{r}_2} + \\ + \sum_n \varphi_n(\vec{r}_1) \, f_{in}(\vec{v}, \vec{n}_2) \, \dfrac{e^{ik_n r_2}}{k_n r_2}, & r_2 \to \infty, \\ \sum_n \varphi_n(\vec{r}_2) \, g_{in}(\vec{v}, \vec{n}_1) \, \dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty; \end{cases} \tag{1}$$

where $\psi_n(\vec{r})$ satisfies the equation /42

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\varphi_n = E_n\varphi_n, \tag{2}$$

and the wave magnitudes k_n are determined from the law of conservation of energy.

$$\frac{k_n^2}{2} + E_n = E. \tag{3}$$

The scattering amplitude $f_{ij}(\vec{v}_1, \vec{v}_2)$ determines, at the given total energy, the probability for scattering of a particle with direction $\vec{v}_1$ to a new direction $\vec{v}_2$ with the atom making the transition from the i state into the j state. The amplitudes g_{ij} determine analogously the probability of an inelastic exchange scattering. The differentially effective cross-section of the inelastic scattering is determined by the formula

$$\sigma_{ij}(\vec{v}_1, \vec{v}_2) = \frac{1}{k_i k_j}|f_{ij}(\vec{v}_1, \vec{v}_2)|^2. \tag{4}$$

Integrating with respect to $\vec{v}_2$ (the direction of the scattered electron) we obtain a complete cross-section for the given inelastic process

$$\sigma_{ij}(\vec{v}) = \frac{1}{k_i k_j}\int |f_{ij}(\vec{v}, \vec{v}')|^2 \, d\omega'. \tag{5}$$

Finally, the complete cross-section of scattering will be obtained after the summation by all possible final states, taking into consideration the exchange.

$$\sigma_i(\vec{v}) = \frac{1}{k_i}\sum_j \frac{1}{k_j}\left[\int |f_{ij}(\vec{v}, \vec{v}')|^2 \, d\omega' + \int |g_{ij}(\vec{v}, \vec{v}')|^2 \, d\omega'\right]. \tag{6}$$

Equations (4)-(6) are true if we consider both electrons as distinguishable particles; that is if, for instance, the projections of the spins of the bombarding and atomic electrons on the z axis equal, respectively, + 1/2 and - 1/2. A calculation of the symmetry of the wave function can be accurately conducted exactly as was done in Section 7, and we will obtain, for instance, the following formula for a complete cross-section which is neutralized /43 by the spins of both electrons:

$$\sigma_i(\vec{v}) = \frac{1}{k_j}\sum_j\left[\frac{1}{4}\int|f^{+}_{ij}(\vec{v},\vec{v}')|^2\,d\omega' + \frac{3}{4}\int|f^{-}_{ij}(\vec{v},\vec{v}')|^2\,d\omega'\right] =$$

$$= \frac{1}{k_i}\sum_j\frac{1}{k_j}\left[\frac{1}{4}\int|f_{ij}(\vec{v},\vec{v}') + g_{ij}(\vec{v},\vec{v}')|^2\,d\omega' +\right.$$

$$\left. + \frac{3}{4}\int|f_{ij}(\vec{v},\vec{v}') - g_{ij}(\vec{v},\vec{v}')|^2\,d\omega'\right]. \qquad (7)$$

The symmetrization of the wave functions $\Psi^{(i)\pm}$ might also be obtained from the function $\Psi^{(i)}$ by formula (7.11).

Let us assume that equation (3) can be carried out only when $i \leq N$, that is

$$E_{N+1} < E. \qquad (8)$$

Then, the energy of the bombarding electrons is sufficient to excite only the first N-1 levels, ionization of the atoms is impossible, and sums by J and n in formulae (1), (6), and (7) contain only a finite number of terms. If, on the other hand, the energy of the electrons is sufficient to ionize the atom then, in addition to the summarization by the discrete states, the integration by the states of the solid spectrum should be conducted in these formulae.

We will examine an inelastic scattering of electrons which is characterized by the amplitude $f_{ij}(\vec{v}_1,-\vec{v}_2)$. Then the wave function $\Psi_1^{(i)}$, which corresponds to the original state and which is substituted in the right part of the functional, should have an asymptotic form (1) with $\vec{v} = v_1$. In accordance with the rule which was brought out in Section 6, the wave function Ψ_2, which corresponds to the final state, should have the following asymptotic form:

$$\Psi_2^{(j)} \sim \begin{cases} \psi_j^* (\vec{r}_1)\, e^{-ik_j \vec{v}_2 \cdot \vec{r}_2} + \\ + \sum_n \psi_n^* (\vec{r}_1)\, f'_{jn} (-\vec{v}_2, \vec{n}_2)\, \dfrac{e^{ik_n r_2}}{k_n r_2}, & r_2 \to \infty, \\ \sum_n \psi_n^* (\vec{r}_2)\, g'_{jn} (-\vec{v}_2, \vec{n}_1)\, \dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty. \end{cases} \tag{9}$$

We will calculate the variation of the functional /44

$$I = \iint \Psi_2^{(j)}\, L\, \Psi_1^{(i)}\, d\tau_1 d\tau_2, \tag{10}$$

where the operator L has the same form as in Section 7. We will, thereby, assume that in the asymptotic solutions of (1) and (9) only the amplitudes f_{ij} and g_{ij} vary. The convergence of the functional of the variated functions $\tilde{\Psi}_1^{(i)}$, $\tilde{\Psi}_2^{(j)}$ can be proved in the same way as was done in Section 7. Essential in the given case is the fact that the complete energy of the states, which corresponds to each term of the asymptotic resolution, is identical. Mainly, thanks to this fact and as a consequence of the orthogonality of the atomic functions $\psi_i (\vec{r})$, all divergent parts in integral (10) are eliminated.

The variation δI is also accurately calculated in the same way as was done in Section 7; however, during substitution of asymptotic functions Ψ_1, Ψ_2 into formula (7.18) it is necessary to utilize the formulae (1) and (9).

After substitution, we obtain

$$\delta I = \lim_{\substack{R_1 \to \infty \\ R_2 \to \infty}} \left\{ \int_{r_1 \leq R_1} d\tau_1 \int_{r_2 \leq R_2} \left[\left(\psi_j^* (\vec{r}_1) e^{-ik\vec{v}_2 \cdot \vec{r}_2} + \right.\right.\right.$$

$$\left.\left.\left. + \sum_n \psi_n^* (\vec{r}_1)\, f'_{jn} (-\vec{v}_2, \vec{n}_2)\, \frac{e^{ik_n r_2}}{k_n r_2} \right) x \right.$$

$$\times \frac{\partial}{\partial r_2}\left(\sum_m \psi_m(\vec{r}_1)\,\delta f_{im}(\vec{v}_1, \vec{n}_2)\,\frac{e^{ik_m r_2}}{k_m r_2}\right) -$$

$$-\left(\sum_m \psi_m(\vec{r}_1)\,\delta f_{im}(v_1, n_2)\,\frac{e^{ik_m r_2}}{k_m r_2}\right)\times$$

$$\times \frac{\partial}{\partial r_2}\left(\psi_j^*(\vec{r}_1)\,e^{-ik\vec{v}_2\cdot\vec{r}_2} + \sum_n \psi_n^*(\vec{r}_1)\,f'_{jn}(-\vec{v}_2, \vec{n}_2)\,\frac{e^{ik_n r_2}}{k_n r_2}\right)\Bigg]\,dS_2 +$$

$$+\int_{r_2<R_2} d\tau_2 \int_{r_1=R_1}\left[\left(\sum_n \psi_n^*(\vec{r}_2)\,g'_{jn}(-\vec{v}_2, \vec{n}_1)\,\frac{e^{ik_n r_1}}{k_n r_1}\right)\times\right.$$

$$\times \frac{\partial}{\partial r_1}\left(\sum_m \psi_m(\vec{r}_1)\,\delta g_{im}(\vec{v}_1, \vec{n}_1)\,\frac{e^{ik_m r_1}}{k_m r_1}\right) - \qquad \underline{/45}$$

$$-\left(\sum_m \psi_m(\vec{r}_1)\,\delta g_{im}(\vec{v}_1, \vec{n}_1)\,\frac{e^{ik_m r_1}}{k_m r_1}\right)\times$$

$$\left.\times \frac{\partial}{\partial r_1}\left(\sum_n \psi_n(\vec{r}_2)\,g'_{jn}(-\vec{v}_2, \vec{n}_1)\,\frac{e^{ik_n r_1}}{k_n r_1}\right)\right]\,dS_1\Bigg\}. \qquad (11)$$

It is easily convincing that during the transition to the limit some of the terms eliminate themselves reciprocally, and part disappears as a result of the orthogonality of the function ψ_j. In the final calculation a non-zero contribution is given only by the term

$$\psi_j^*(\vec{r}_1)\,e^{-ik_j\vec{v}_2\cdot\vec{r}_2} \qquad (12)$$

and the function $\psi_2^{(j)}$ and the term

$$\psi_j(\vec{r}_1)\,\delta f_{ij}(\vec{v}_1, \vec{n}_2)\,\frac{e^{ik_j r_2}}{k_j r_2} \qquad (13)$$

and the function $\delta\Psi_1^{(i)}$. Calculation of the integral is conducted exactly as in Section 7 and we obtain

$$\delta I = -\frac{4\pi}{k_j}\,\delta f_{ij}\,(\vec{v}_1, \vec{v}_2). \tag{14}$$

If we exchange positions of the arguments, $\vec{r}_1$ and $\vec{r}_2$ in the function $\Psi_2^{(j)}$, then we obtain, analogously

$$\delta I = \delta \iint \Psi_2^{(j)}\,(\vec{r}_2, \vec{r}_1)\; L\; \Psi_1^{(i)}\,(\vec{r}_1, \vec{r}_2)\; d\tau_1 d\tau_2 =$$

$$= -\frac{4\pi}{k_j}\,\delta g_{ij}\,(\vec{v}_1, \vec{v}_2). \tag{15}$$

From these formulae we immediately obtain formulae which are analogous to (7.21) for symmetrized functions and amplitudes.

It was assumed up to now that the atomic wave functions Ψ_i in the asymptotic expression for $\Psi_1^{(i)}$ and $\Psi_2^{(j)}$ do not variate. Just as was done in the case of elastic scattering, this formula can be generalized in the case of the variation of the function ψ_i. The convergence of the functional from the variated functions in this case can be assured if, simultaneously with the change in the function ψ_i, we also change /46 the wave numbers k_i in such a manner that we preserve the equalities

$$\int \tilde{\psi}_i^{*}\,(\vec{r})\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\tilde{\psi}_i\,(\vec{r})\,d\tau + \frac{k_i^2}{2} = E. \tag{16}$$

In that case, the divergent numbers in the subintegral expression disappear. If, in addition, the conditions of orthogonality and standardization are carried out in the case of the variated functions as was done before, then the expression for the variation δI remains unchanged. This type of variation should be considered if the atomic functions ψ_i are not accurately known. Investigation of this type of variation is also necessary with the conclusion drawn from the virial theorem (see Chapter IV).

In the process of formulating the variational principle for this given problem we have, in fact, never utilized the concrete properties of the hydrogen atom. Therefore, the formulation of the variational principle (14) represents a general formulation for arbitrary inelastic collisions.

Thus, by formulating the variational principle for various specific cases, we obtain certain functionals, which are stationary in relation to a broad class of variations, in the case when the variated functions satisfy the Schroedinger equation. To be exact, these values of physical interest, in this case, prove to be stationary, i.e., the phases and amplitudes of scattering just as in the case of a discrete spectrum when the average energy of the atomic system was stationary. Such a circumstance is particularly essential during the development of approximate methods for the calculation of all these values.

The investigated formulation of the variational principle for elastic and inelastic collisions in this chapter was briefly discussed in the paper by Kohn (Ref. 15). This same formulation for concrete problems of collisions between electrons with hydrogen atoms was presented later in the paper by Gordon and Jones (Ref. 37).

The possibility of variation of atomic wave functions in an asymptotic form of a complete wave function was discussed in the dissertation by this author (Ref. 38).

CHAPTER II

/47

RELATION BETWEEN VARIOUS FORMULATIONS OF VARIATIONAL PRINCIPLES AND THEIR APPLICATION IN COLLISION THEORY

§9. Relation Between The Variational Principles By Hulthen and Kohn

We will prove that the formulations of the variational principle in Section 3 and in Section 6 are equivalent, if the potential V (r) is spherically symmetrical; that is, if the forces are of a central nature.

In that case, the functions Ψ_1 and Ψ_2 in the functional (6.8) may be resolved with the Legendre polynomials, as was done in Section 4 (4.3). In the case of the variated functions $\tilde{\Psi}_i$, we obtain

$$\tilde{\Psi}_i = \Psi_i + \delta\Psi_i =$$

$$= \sum_{l=0}^{\infty} (2l + 1)\, i^l e^{i(\eta_l + \delta\eta_l)} \frac{1}{kr} (\psi_l + \delta\psi_l)\, P_l (\vec{v}_i \cdot \vec{n}). \qquad (1)$$

The solution of the variated scattering amplitude f is obtained from formula (4.4)

$$\tilde{f}_i = f_i + \delta f_i =$$

$$= \frac{1}{2i} \sum_{l=0}^{\infty} (2l + 1)\, i^l \left[e^{2i(\eta_l + \delta\eta_l)} - 1 \right] P_l (\vec{v}_i \cdot \vec{n}). \qquad (2)$$

We will substitute the solution to the function $\tilde{\Psi}_i$ in the /48 functional (6.8) and we will separate the integration with respect to the angles.

$$I(\tilde{\Psi}_2, \tilde{\Psi}_1) = \sum_{\ell,\ell'=0} (2\ell + 1)\ (2\ell' + 1)\ \frac{1}{k^2}\ i^{\ell+\ell'}\ e^{i(\eta_\ell+\eta_{\ell'}+\delta\eta_\ell+\delta\eta_{\ell'})}\ x$$

$$x \int_0^\infty (\psi_\ell + \delta\psi_\ell) \left[\frac{d^2}{dr^2} + k^2 - V(r) - \frac{\ell'\ (\ell' + 1)}{r^2}\right] (\psi_{\ell'} + \delta\psi_{\ell'})\ dr\ x$$

$$x \int P_\ell\ (\vec{v}_1 \cdot \vec{n})\ P_\ell(\vec{v}_2 \cdot \vec{n})\ d\omega. \qquad (3)$$

In the last integral the integration is conducted with respect to all directions of the unit vector $\vec{n}$ which can easily be calculated if we utilize the theorem for addition for the Legendre polynomials

$$\int P_\ell\ (\vec{v}_1 \cdot \vec{n})\ P_{\ell'}\ (\vec{v}_2 \cdot \vec{n})\ d\omega = \frac{4\pi}{2\ell + 1}\ P_\ell\ (\vec{v}_1 \cdot \vec{v}_2) \cdot \delta_{\ell\ell'}. \qquad (4)$$

The radial integral in the expression of (3) converts into zero in the case of the invariant functions ψ_ℓ. Therefore, during the calculation of δI it is not necessary to take into consideration the phase variation in the exponential multiplier. We will obtain

$$\delta I = \sum_{\ell=0}^{\infty} (2\ell + 1)\ (-)^\ell\ e^{2i\eta_\ell}\ k^{-2}\ 4\pi\ P_\ell\ (\vec{v}_1 \cdot \vec{v}_2)\ x$$

$$x \int (\psi_\ell + \delta\psi_\ell) \left(\frac{d^2}{dr^2} + k^2 - V - \frac{\ell\ (\ell + 1)}{r^2}\right) (\psi_\ell + \delta\psi_\ell)\ dr. \qquad (5)$$

On the other hand: as a result of formula (2), the variation δf may be stated as follows:

$$\delta f\ (\vec{v}_1, -\vec{v}_2) = \sum_{\ell=0}^{\infty} (2\ell + 1)\ e^{2i\eta_\ell}\ \delta\eta_\ell\ P_\ell(\vec{v}_1, -\vec{v}_2) =$$

$$= \sum_{\ell=0}^{\infty} (2\ell + 1)\ e^{2i\eta_\ell}\ \delta\eta_\ell\ (-)^\ell\ P_\ell\ (\vec{v}_1 \cdot \vec{v}_2). \qquad (6)$$

We will utilize the variational principle as formulated by Hulthen. The radial integral in formula (5), according to (4.29) will equal - /49 $k\delta\eta_\ell$, and we will thus obtain formula (6.16)

$$\delta I = - \frac{4\pi}{k} \delta f (\vec{v}_1, - \vec{v}_2). \tag{7}$$

Vice versa, by substituting in formula (7) the solution of (1) and (2) and by comparing the coefficients at identical Legendre polynomials, we obtain the formula (4.29)

$$\int (\psi_\ell + \delta\psi_\ell) \left(\frac{d^2}{dr^2} + k^2 - V - \frac{\ell(\ell+1)}{r^2}\right) (\psi_\ell + \delta\psi_\ell)\, dr =$$

$$= - k\delta\eta_\ell. \tag{8}$$

In an analogous way more complicated cases can also be proved. We will examine, for instance, excitation of the first (2s) level of a hydrogen atom by an electron with a moment of 0, that is by its s-wave. If we consider the electrons to be distinguishable, then the wave functions Ψ_1, Ψ_2 will have the following asymptotic form;

$$\Psi_1^{(0)} \sim \begin{cases} \psi_0(r_1)\, e^{ik_0 \vec{v}_1 \cdot \vec{r}_2} + \sum_n f_{0n}(\vec{v}_1, \vec{n}_2)\, \psi_n(\vec{r}_1)\, \dfrac{e^{ik_n r_2}}{k_n r_2}, & \\ & r_2 \to \infty, \\ \sum_n g_{0n}(\vec{v}_1, \vec{n}_1)\, \psi_n(\vec{r}_2)\, \dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty; \end{cases} \tag{9}$$

$$\Psi_2^{(1)} \sim \begin{cases} \psi_1^*(r_1)\, e^{ik_1 \vec{v}_2 \cdot \vec{r}_2} + \sum_n f'_{\ell 1}(\vec{v}_2, \vec{n}_2)\, \psi_n^*(\vec{r}_1)\, \dfrac{e^{ik_n r_2}}{k_n r_2}, & \\ & r_2 \to \infty, \\ \sum_n g'_{\ell 1}(\vec{v}_2, \vec{n}_1)\, \psi_n(\vec{r}_2)\, \dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty. \end{cases} \tag{10}$$

If we resolve these functions with respect to partial waves and if we define the resolution coefficients of this scattering amplitude f_{0n}, g_{0n}, f'_{1n}, g'_{1n} by the Legendre polynomials, respectively, through c_{0n}, /50 d_{0n}, c'_{1n}, d'_{1n}, then the wave function for the s-scattering will have the following asymptotic form:

$$\psi_{1S}^{(0)} \sim \begin{cases} \psi_0(r_1)\dfrac{\sin k_0 r_2}{k_0 r_2} + \sum_n^S C_{0n}\psi_n(r_1)\dfrac{e^{ik_n r_2}}{k_n r_2}, & \\ & r_2 \to \infty, \\ \sum_n^S d_{0n}\psi_n(r_2)\dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty; \end{cases} \tag{11}$$

$$\psi_{2S}^{(1)} \begin{cases} \psi_1^*(r_1)\dfrac{\sin k_1 r_2}{k_1 r_2} + \sum_n^S C'_{1n}\psi_n^*(r_1)\dfrac{e^{ik_n r_2}}{k_n r_2}, & \\ & r_2 \to \infty, \\ \sum_n^S d'_{1n}\psi_n^*(r_2)\dfrac{e^{ik_n r_1}}{k_n r_1}, & r_1 \to \infty, \end{cases} \tag{12}$$

whereby in the formulae of (11) and (12) the summarization is conducted only in respect to the s-state of hydrogen. From the variational principle for inelastic processes, which was formulated in Section 8, we obtain

$$\delta \iint \psi_2^{(1)} \left(\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}} + k_0^2 - 1\right) \psi_1^{(0)}\, d\tau_1\, d\tau_2 =$$

$$= -\frac{4\pi}{k_1}\delta f_{01}(\vec{v}_1, -\vec{v}_2). \tag{13}$$

From this, we easily obtain:

$$\delta \iint \psi_{2s}^{(1)} \left(\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} + \frac{2}{r_{12}} + \right.$$

$$\left. + k_0^2 - 1 \right) \psi_{1s}^{(0)} \, d\tau_1 \, d\tau_2 = - \frac{4\pi}{k_i} \delta C_{01} \, . \qquad (14)$$

This formula can also be easily obtained directly by calculating the functional $I(\psi_{2s}^{(1)}, \psi_{1s}^{(0)}$ and by utilizing Green's formula.

In such a form the variational principle is convenient only for concrete additions, since, in practice, variational calculations are /51 conducted only in the case of slow collisions in which the first partial waves ($\ell = 0.1$) play the principal role.

The relation between the variational principles of Hulthen and Kohn investigated here was mentioned in the works of (Ref. 37 and 39).

§10. The Variational Principle and the Excitation Theory

It is a well known fact that the principal formulae in the stationary theory of excitation from related states might be derived from the variational principle. Analogous results can also be obtained in the theory of collisions from the scattering amplitudes and phases, if based on the stationarity of the corresponding functionals.

Let us examine the equation:

$$(\nabla^2 + k^2 - V_0 - \lambda V) \, \psi \, (\vec{r}) = 0, \qquad (1)$$

where the operators V_0 and V should satisfy the same conditions as did the operator V during the derivation of the variational principle. The operator λV will be considered by us as excitation. The solution to this equation depends on the parameter λ and should have the following asymptotic form:

$$\psi(\lambda, \vec{v}, \vec{r}) \sim e^{ik\vec{v}\cdot\vec{r}} + f \, (\lambda, \vec{v}, \vec{n}) \, \frac{e^{ikr}}{kr} \, . \qquad (2)$$

We will resolve the functions ψ and f into a series along λ degrees.

$$\psi\ (\lambda, \vec{v}, \vec{r}) = \psi_0\ (\vec{v}, \vec{r}) + \lambda\psi_1\ (\vec{v}, \vec{r}) + \\ + \cdot\ \cdot\ \cdot + \lambda^n\psi_n\ (\vec{v}, \vec{r}) + \cdot\ \cdot\ \cdot\ , \tag{3}$$

$$f\ (\lambda, \vec{v}, \vec{n}) = f_0\ (\vec{v}, \vec{n}) + \lambda f_1\ (\vec{v}, \vec{n}) + \\ + \cdot\ \cdot\ \cdot + \lambda^n f_n\ (v, n) + \cdot\ \cdot\ \cdot\ . \tag{4}$$

Then, for the function ψ_n, we obtain the system of equations:

$$(\nabla^2 + k^2 - V_0)\ \psi_0 = 0, \tag{5}$$

$$(\nabla^2 + k^2 - V_0)\ \psi_n = V\psi_{n-1} \qquad (n = 1, 2, \cdot\ \cdot\ \cdot) \tag{6}$$

and these equations will have the following asymptotic form: /52

$$\psi_0 \sim e^{ik\vec{v}\cdot\vec{r}} + f_0\ (\vec{v}, \vec{n})\ \frac{e^{ikr}}{kr}\ , \quad \psi_n \sim f_n\ (\vec{v}, \vec{n})\ \frac{e^{ikr}}{kr}\ . \tag{7}$$

If we should limit ourselves to the n + 1 term in the succession of formulae (3) and (4), then we obtain the approximate functions:

$$\psi^{(n)}\ (\lambda, \vec{v}, \vec{r}) = \sum_{i=0}^{n} \lambda^i \psi_i\ (\vec{v}, \vec{r})\ , \tag{8}$$

$$f^{(n)}\ (\lambda, \vec{v}, \vec{n}) = \sum_{i=1}^{n} \lambda^i f_i\ (\vec{v}, \vec{n})\ , \tag{9}$$

which we will call, respectively, the wave function and the scattering amplitude in the n^{th} approximation.

We will assume that the series (3) and (4) for the functions for ψ and f converge. This takes place if λ is sufficiently small, k is sufficiently large, and the operator V decreases sufficiently fast with the increase of r. A rigorous examination of the convergence of such series has been conducted so far only in the most simple cases (see, for instance, Ref. 40).

We will assume now that the solution to the unexcited equation (5) with its asymptotic form (7) is known to us in the case of all values of the vector $\vec{k} = k\vec{v}$, and also for the related states ($k_n^2 2 = E_n < 0$).

Then we are able to construct Green's function $G(k; \vec{r}, \vec{r}')$ for the operator $\nabla^2 + k^2 - V_0$, which satisfies the equation:

$$(\nabla^2 + k^2 - V_0)\, G(k; \vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'). \tag{10}$$

The solution to this equation may be stated as follows:

$$G(k; \vec{r}, \vec{r}') =$$

$$= \frac{1}{(2\pi)^3} \int_0^\infty \frac{dk'^2}{k^2 - k'^2} \int \psi_0^* (k', \vec{v}, \vec{r})\, \psi_0 (k', \vec{v}, \vec{r})\, d\omega +$$

$$+ \sum_n \frac{\psi_0^* (E_n, \vec{r}')\, \varphi_0 (E_n, \vec{r})}{k^2 - E_n}, \tag{11}$$

where the internal integration is conducted with respect to all directions of the unit vector $\vec{v}$ and, during the integration by k, the integral should be considered as a contour integration in the complex plane k', and should exclude the pole at the point k' = k.* Only with such a selection of the integration method can we obtain a solution to the heterogenic equation which, in the presence of large r, contains only divergent waves. The function of the related states $\psi_0 (E_n, \vec{r})$ satisfies the equations:

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*In the case when the energy operator H has only a discrete spectrum, $H\psi_n = E_n\psi_n$, then Green's function will have the following form: $G(E; \vec{r}, \vec{r}') = \sum_n \psi_n^* (\vec{r}')\, \psi_n (\vec{r})/(E_n - E)$. When $E = E_m$, the m-diverging term of the sum is excluded. This requirement is analogous to selecting a path during the integration with respect to k' in the formula (11).

$$(\nabla^2 + E_n - V_0)\ \psi_0\ (E_n, \vec{r}) = 0. \tag{12}$$

By utilizing Green's function we are able to transfer the last term of equation (1) to the right hand side and, considering this term as being formally heterogenic, we can state the solution in the following form:

$$\psi\ (\vec{r}) = \psi_0\ (\vec{r}) + \lambda \int G\ (\vec{r}, \vec{r}')\ V\ (\vec{r}')\ \psi\ (\vec{r}')\ d\tau'. \tag{13}$$

We will solve the resulting integral equation with the method of consecutive approximations, using the function ψ_0 in the capacity of a null approximation. We will thereby automatically obtain a series resolution by λ° up to λ^n, for the n-approximation.

Thus, during solution of the integral equation the n-approximation coincides with the wave function $\psi^{(n)}$ in formula (5). As far as the n-term of the series solution is concerned, we obtain the recurrent formula:

$$\psi_n\ (\vec{r}) = \int G\ (\vec{r}, \vec{r}')\ V\ (\vec{r}')\ \psi_{n-1}\ (\vec{r}')\ d\tau'$$

$$(n = 1, 2, \cdots). \tag{14}$$

We will now show how to obtain an expression for $f_n\ (\vec{v}, \vec{n})$ by utilizing the variational principle. For this purpose we will examine the functional (6.19):

$$J\ (\varphi_2, \varphi_1) =$$

$$= g_1\ (-\vec{v}_2) + \frac{k}{4\pi} \int \varphi_2\ (\nabla^2 + k^2 - V_0 - \lambda\ V_1)\ \varphi_1\ d\tau, \tag{15}$$

the stationarity of which was proven in Section 6. We will mention /54 that, during the calculation of the variation of this functional, we have disregarded the integral $\int \delta\varphi_2\ (\nabla^2 + k^2 - V_0 - \lambda V)\ \delta\varphi_1 d\tau$ in formula (6.11). This expression reduces to zero if either $\delta\varphi_1$, $\delta\varphi_2$ equals zero, which proves

that $J(\varphi_2, \varphi_1)$ will yield an accurate value for the scattering amplitude even in that case when only the accurate solution to equation (1) was substituted instead of one of the functions φ_1 or φ_2. In that case the second function might be any given function; it is required only that this function should have a proper asymptotic form (6.18).

We will substitute in functional (15), instead of φ_2, the accurate solution $\psi(\vec{v}_2, \vec{r})$ and, instead of φ_1, we will substitute the solution $\psi_0(\vec{v}_1, \vec{r})$. Then, by utilizing (5) we obtain:

$$f(\lambda_1, \vec{v}_1, -\vec{v}_2) = f_0(\vec{v}_1, -\vec{v}_2) - \\ - \frac{\lambda k}{4\pi} \int \psi(\vec{v}_2, \vec{r}) V(\vec{r}) \psi_0(\vec{v}_1, \vec{r}) d\tau. \qquad (16)$$

Analogous correlations in which the scattering amplitude of the phase is expressed by an integral which contains the accurate wave function might be obtained for any given problem in collision theory. These correlations are known as common integral identities and are broadly used in theory and in numerical calculations. In all cases the integral identities are obtained immediately from the corresponding variational principle using the same methods as in equation (16).

By substituting solution (3) in formula (16), we obtain*:

$$f_n(\vec{v}_1, -\vec{v}_2) = -\frac{k}{4\pi} \int \psi_{n-1}(\vec{v}_2, \vec{r}) V(\vec{r}) \psi_0(\vec{v}_1, \vec{r}) d\tau, \qquad (17)$$

$$f^{(n)}(\vec{v}_1, -\vec{v}_2) = f_0(\vec{v}_1, -\vec{v}_2) - \\ - \frac{\lambda k}{4\pi} \int \psi^{(n-1)}(\vec{v}_2, \vec{r}) V(\vec{r}) \psi_0(\vec{v}_1, \vec{r}) d\tau. \qquad (18)$$

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*Henceforth, the functions under the integrals will not be provided with the symbols 1 and 2 in this and the following sections; the function on the right side will correspond to the value $\vec{v} = \vec{v}_2$, and the function on the left will correspond to the value $\vec{v} = \vec{v}_1$.

We will now substitute in the functional (15), instead of /55 φ_2, the function $\psi_2 = \psi^{(m)}(\vec{v}_2, \vec{r})$, and instead of φ_1, we will substitute the function $\psi_1 = \psi^{(n)}(\vec{v}_1, \vec{r})$. Then, by utilizing equations (5) and (6), we will obtain

$$J(\psi^{(m)}, \psi^{(n)}) =$$

$$= f^{(n)}(\vec{v}_1, -\vec{v}_2) + \frac{\lambda k}{4\pi}\int \psi^{(m)}(\nabla^2 + k^2 - V_0 - \lambda V)\psi^{(n)} d\tau =$$

$$= f^{(n)}(\vec{v}_1, -\vec{v}_2) - \frac{\lambda^{n+1} k}{4\pi}\int \psi^{(m)} V\psi_n d\tau. \qquad (19)$$

In that case the expression obtained will be polynomial in relation to λ of degree $m + n + 1$; the variations J of the integral $\int \delta\psi_2 (\nabla^2 + k^2 - V_0 - \lambda V)\delta\psi_1 d\tau$, which were dropped during the calculation of the variation J, will be on the order of λ^{m+n+2} and, thus:

$$f^{(m+n+1)}(\vec{v}_1, \vec{v}_2) = f^{(n)}(\vec{v}_1, -\vec{v}_2) - \frac{\lambda^{n+1} k}{4\pi}\int \psi^{(m)} V\psi_n d\tau; \qquad (20)$$

$$f_{m+n+1}(\vec{v}_1, -\vec{v}_2) =$$

$$= -\frac{k}{4\pi}\int \psi_m(\vec{v}_2, \vec{r}) V(\vec{r}\ \psi_n(\vec{v}_1, \vec{r}) d\tau. \qquad (21)$$

That same result can also be obtained directly, of course, by utilizing equations (6) and (17) and the condition:

$$\int \psi_m(\vec{v}_1, \vec{r})(\nabla^2 + k^2 - V_0)\psi_n(\vec{v}_2, \vec{r}) d\tau =$$

$$= \int \psi_n(\vec{v}_2, \vec{r})(\nabla^2 + k^2 - V_0)\psi_m(\vec{v}_1, \vec{r}) d\tau, \qquad (22)$$

$$m, n = 1, 2, 3, \ldots$$

In this manner we can see that by knowing the function $\psi(\vec{v}_2, \vec{r})$ in the m^{th} approximation, and the function $\psi(\vec{v}_1, \vec{r})$ in the n^{th} approximation, it is possible for us to obtain the expression for f in the approximation $m + n + 1$.

Of particular significance for numerical calculations is the first approximation in the theory of excitations. In that case the expression for the scattering amplitude has the following form

$$f^{(1)}(\vec{v}_1, -\vec{v}_2) =$$

$$= f_0(\vec{v}_1, -\vec{v}_2) - \frac{\lambda k}{4\pi}\int \psi_0(\vec{v}_2, \vec{r})\, V\, \psi_0(\vec{v}_1, \vec{r})\, d\tau, \qquad (23)$$

and it is necessary to know, for calculation purposes, only two unexcited wave functions for these values of $\vec{v}$ which are included in the desired amplitude. Both of the following approximations in the formula for the scattering amplitude included Green's function, the determination of which in the case of the unexcited operator, $\nabla^2 + k^2 - V_0$, is usually a very complicated problem. /56

We will now examine a very important specific case when the entire potential energy operator may be considered as excited. In that case

$$V_0 = 0, \quad \psi_0 = e^{ik\vec{v}\cdot\vec{r}}, \quad f_0 = 0, \qquad (24)$$

Green's function for the unexcited problem (the operator $\nabla^2 + k^2$) can be calculated in this obvious form

$$G(\vec{r}, \vec{r}') = -\frac{1}{4\pi}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r} - \vec{r}'|}. \qquad (25)$$

In the theory of excitation, the method of successive approximations is known as the born method. Particularly in the first and second approximations, we obtain

$$f_b^{(1)} = -\frac{\lambda k}{4\pi}\int e^{-ik\vec{v}_2\cdot\vec{r}}\, V e^{ik\vec{v}_1\cdot\vec{r}}\, d\tau, \qquad (26)$$

$$f_b^{(2)} = f_b^{(1)} + \frac{\lambda^2 k}{(4\pi)^2} \int e^{-ik\vec{v}_2 \cdot \vec{r}} V(\vec{r}) \times$$

$$\times \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} V(r') e^{ik\vec{v}_1 \cdot \vec{r}} d\tau_1 d\tau_2. \qquad (27)$$

If the operator V(r) is spherically symmetrical, then in formula (26) the angular integration can be easily carried out and we then have

$$f_b^{(1)} = -k\lambda \int_0^\infty \frac{\sin qr}{qr} V(r) r^2 dr, \qquad (28)$$

where $\vec{q} = k(\vec{v}_2 - \vec{v}_1)$, and $q = |\vec{q}|$. Finally, the accurate formula for the scattering amplitude (16) will have the following form

$$f(\vec{v}_1, -\vec{v}_2) = -\frac{\lambda k}{4\pi} \int \psi(\vec{v}_2, \vec{r}) V e^{ik_1 \vec{v} \cdot \vec{r}} d\tau. \qquad (29)$$

All formulae obtained here are for a three dimensional problem./57 However, if the operators V_0 and V are spherically symmetrical, then the analogous considerations and formulas are suitable for a one dimensional equation

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - V_0(r) - \lambda V(r)\right] \psi(r) = 0, \qquad (30)$$

$$\psi(0) = 0, \quad \psi \sim \sin\left(kr - \frac{l\pi}{2} + \eta\right); \qquad (31)$$

if the solution to the unexcited equation is known

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - V_0(r)\right] \psi_0(r) = 0, \qquad (32)$$

$$\psi_0(0) = 0, \quad \psi_0 = \sin\left(kr - \frac{l\pi}{2} + \eta_0\right). \qquad (33)$$

By utilizing the variational principle which was formulated in Section 4, it is possible to repeat all considerations of this section for a one dimensional problem. The phase expression in the first approximation will have, for instance, the following form

$$\eta^{(1)} = \eta_0 - \frac{\lambda}{k} \int_0^\infty (\psi_0 \, r) \, V\psi_0 \, (r) \, dr. \tag{34}$$

In the Born approximation

$$V_0 = 0, \quad \eta_0 = 0, \quad \psi_0 = \sqrt{\frac{\pi kr}{2}} \, I_{\ell+1/2} \, (kr), \tag{35}$$

where I_p (z) are the Bessel functions. Then, in the first approximation

$$\eta_b^{(1)} = - \lambda \cdot \frac{\pi}{2} \int_0^\infty \sqrt{r} \, I_{\ell+1/2} \, (kr) \, V \, (r) \left[\sqrt{r} \, I_{\ell+1/2} \, (kr) \right] dr. \tag{36}$$

If the operator V (r) is a function, then we arrive at the common formula

$$\eta_b^{(1)} = - \lambda \frac{\pi}{2} \int_0^\infty V \, (r) \, I^2_{\ell+1/2} \, (kr) \, r \, dr. \tag{37}$$

We will mention that in collision theory the basic formulae /58 for successive approximations and the theory of excitation have a much simpler form than analogous formulae for related states. This is caused by the fact that in the case of problems of a discrete spectrum the heterogenic equation $(H - E) \psi = F$ has a solution only under the condition of orthogonality of the function F toward all solutions of the heterogenic equation $(H - E) \psi_0 = 0$. Therefore, when solving (by means of successive approximations) a system which is analogous to the system in (5), we should always conduct orthogonalization of the right part (from which the energy value of the related state in the following approximation is obtained). In the problem of related states this does not give a possibility to construct a simple recurrent formula for ψ_n, which would be analogous to formula (14). In addition, contrary to the problem of a discrete spectrum of the energy operator, it is not necessary to pay any special attention to the case of degeneration in the collision theory, if only one particle is being considered.

All formulae which were derived in this section may also be generalized for more complicated problems concerning the collision of electrons with atoms: elastic, inelastic, and exchange scattering. Due to the complexity of these problems, a fundamental value must be assumed in the Born method, which quite often permits carrying out calculations in the first approximation to the end. In that case wave functions, which correspond to the initial and final states in the null approximation, are substituted in the stationary functional, that is, in the form of producing a plane wave, which characterizes the bombarding particle, on the wave function of the atom in the proper state.

If we should substitute in the functional wave functions of the null approximation, which were symmetrized beforehand in accordance with the Pauli principle, then we obtain the scattering amplitude in the Born-Oppenheimer approximation. The question on the applicability of the Born method and the Born-Oppenheimer method to the problem of scattering of electrons by atoms is discussed in detail in Ref. 41.

The relation between the variational principle and the Born method was pointed out in many papers (Refs. 12, 16, 29). The formulae in the theory of excitation for a phase were obtained somewhat differently in the paper by Makinson and Turner (Ref. 28). In that same paper /59
expressions were obtained for a phase in the second approximation. However, the formula obtained by them is not analogous to the standard formula for energy in the second approximation and does not permit generalization for more complicated cases.

§11. Variational Principles Based on the Integral Equation for Wave Functions

If we take as a basis the integral equation for a wave function (derived in the preceding section) then it is possible to construct functionals which are stationary in relation to the variation of accurate wave functions; that is, it is possible to obtain a new variational principle. These functionals differ, essentially, from the Hulthen-Kohn functional in Chapter I. Just as before, we will examine equation (10.1) of the preceding section, assuming for simplicity $\lambda = 1$, which does not limit the generality of our reasoning in any way. In order to avoid cumbersome formulae, we will introduce the following simplified definitions for the integrals which contain the wave functions, Green's function (10.10), and the excitation operator:

$$G^n\psi = \int \cdots \int G(\vec{r}, \vec{r}_1)\, V(\vec{r}_1)\, G(\vec{r}_1, \vec{r}_2) \cdots$$

$$\cdots V(\vec{r}_{n-1})\, G(\vec{r}_{n-1}, \vec{r}_n)\, V(\vec{r}_n)\, \psi(\vec{v}, \vec{r}_n)\, d\tau_1, \ldots d\tau_n, \quad (1)$$

$$(\psi_\alpha, \psi_\beta) = \int \psi_\alpha (\vec{v}_2, \vec{r}) V (\vec{r}) \psi_\beta (\vec{v}_1, \vec{r}) d\tau.^* \quad (2)$$

In these definitions, the integral equation (10.13) will have the following form

$$\psi = \psi_0 + G\psi. \quad (3)$$

The scattering amplitude f in formula (10.16) will be as follows

$$f = f_0 - \frac{k}{4\pi} (\psi, \psi_0). \quad (4)$$

Thus, the desired value is (ψ, ψ_0), through which the scattering amplitudes can easily be expressed. If, in the capacity of a null approximation, we use the plane waves and $f_0 = 0$ (the Born method), then (ψ, ψ_0) and f coincide in accuracy with the multiplier. For the scattering amplitude in the n^{th} approximation we obtain in these same definitions /60

$$f^{(n)} = f_0 - \frac{k}{4\pi} [(\psi_0, \psi_0) + (\psi_0, G\psi_0) + \ldots + (\psi_0, G^{n-1} \psi_0)]. \quad (5)$$

We will examine the functional

$$A_n (\psi, \psi) = (\psi, G^n \psi), \quad (6)$$

and we will compute its variation, considering that both functions are accurate solutions to equation (3). We obtain

$$\delta A_n = (\psi, G^n \delta\psi) + (\delta\psi, G^n \psi) = (\psi - \psi_0, G^{n-1} \delta\psi) +$$
$$+ (\delta\psi, G^{n-1} \psi - G^{n-1} \psi_0) = \ldots = (\psi - \psi_0 - \psi_0 G - \ldots$$
$$\ldots - \psi_0 G^{n-1}, \delta\psi) + (\delta\psi, \psi - \psi_0 - G\psi_0 - \ldots - G^{n-1} \psi_0). \quad (7)$$

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*The excitation $V (\vec{r})$ may, in this case, be considered as a wave function during integration.

The right part of this expression is also a complete variation and we find out in this manner that the functionals

$$B_n = (\psi, G^n\psi) - (\psi, \psi) + (\psi, \psi_0 + G\psi_0 + \cdots + G^{n-1}\psi_0) +$$

$$+ (\psi_0 + \psi_0 G + \cdots + \psi_0 G^{n-1}, \psi) \qquad (8)$$

are stationary in relation to the arbitrary variations of accurate wave functions.

We will compute the stationary value of this functional

$$B_n(\psi, \psi) = (\psi, \psi - \psi_0 - G\psi_0 - \cdots - G^{n-1}\psi_0) - (\psi, \psi) +$$

$$+ (\psi, \psi_0 + G\psi_0 + \cdots + G^{n-1}\psi_0) + (\psi_0 + \psi_0 G + \cdots$$

$$\cdots + \psi_0 G^{n-1}, \psi) = (\psi_0, \psi) + (\psi_0, \psi - \psi_0) +$$

$$+ (\psi_0, \psi - \psi_0 - G\psi_0) + \cdots + (\psi_0, \psi - \psi_0 - G\psi_0 - \cdots$$

$$\cdots - G^{n-2}\psi_0) = n(\psi_0, \psi) - (n-1)(\psi_0, \psi_0) -$$

$$- (n-2)(\psi_0, G\psi_0) - \cdots - (\psi_0, G^{n-2}\psi_0). \qquad (9)$$

Now, we will substitute, in this functional, the function ψ_0. We obtain /61

$$B_n(\psi_0, \psi_0) = (\psi_0, \psi_0 + G\psi_0 + \cdots + G^n\psi_0) + (\psi_0, \psi_0 +$$

$$+ G\psi_0 + \cdots + G^{n-1}\psi_0) - (\psi_0, \psi_0) = (\psi, \psi_0)^{(n+1)} +$$

$$+ (\psi, \psi_0)^{(n)} - (\psi_0, \psi_0), \qquad (10)$$

where the expression $(\psi, \psi_0)^{(n)}$ in accordance with formulae (4) and (5) defines the value (ψ, ψ_0) in the n^{th} approximation of the excitation theory. We will now construct the succession of the functionals

$$C_1 = B_1, \quad C_2 = B_2 - B_1, \quad \cdots, \quad C_n = B_n - B_{n-1}, \quad \cdots \qquad (11)$$

It is obvious that these functionals are also stationary in relation to the arbitrary variation of accurate wave functions. By substituting the obvious expressions for B_n in (11), we obtain

$$C_n(\varphi_2, \varphi_1) = (\varphi_2, G^n\varphi_1) - (\varphi_2, G^{n-1}\varphi_1) + \\ + (\varphi_2, G^{n-1}\psi_0) + (\psi_0, G^{n-1}\varphi_1). \quad (12)$$

By utilizing (9) and (10), we obtain the stationary value C_n

$$\text{St}\{C_n\} = C_n(\psi, \psi) = (\psi, \psi_0) - (\psi_0, \psi_0) - (\psi_0, G\psi_0) - \cdots \\ \cdots - (\psi_0, G^{n-2}\psi_0) = (\psi, \psi_0) - (\psi, \psi_0)^{(n-1)} \quad (13)$$

and the approximate value

$$C_n(\psi_0, \psi_0) = (\psi, \psi_0)^{(n+1)} - (\psi, \psi_0)^{(n-1)}. \quad (14)$$

Thus, we finally find out that the functionals

$$D_n = f_0 - \frac{k}{4\pi}[(\varphi_2, G^n\varphi_1) - (\varphi_2, G^{n-1}\varphi_1) + (\varphi_2, G^{n-1}\psi_0) + \\ + (\psi_0, G^{n-1}\varphi_1) + (\psi_0, \psi_0) + (\psi_0, G\psi_0) + \cdots \\ \cdots + (\psi_0, G^{n-2}\psi_0)] \quad (15)$$

are stationary in relation to the variation of accurate wave functions and have, in the capacity of a stationary value, an accurate /62
scattering amplitude. If we should substitute in this functional a wave function of a null approximation, then we obtain a scattering amplitude in the approximation (n + 1).

An even more simple and symmetrical functional F_n is obtained for the correction toward the scattering amplitude in the (n + 1) approximation

$$F_n(\varphi_2, \varphi_1) = -\frac{k}{4\pi}\left[(\varphi_2, G^n \varphi_1) - (\varphi_2, G^{n-1}\varphi_1) + \right.$$

$$\left. + (\varphi_2, G^{n-1}\psi_0) + (\psi_0, G^{n-1}\varphi_1) - (\psi_0, G^{n-1}\psi_0)\right];$$

$$f_{n+1} = F_n(\psi_0, \psi_0); \quad f - f^{(n)} = St\{F_n\}. \tag{16}$$

We will now prove that if in the functional D_n we substitute the function of p-approximation $\psi^{(p)} = (1 + G + \cdots + G^p)\psi_0$ for the function φ_1, and instead of φ_2 we substitute the function of the q-approximation $\psi^{(q)} = (1 + G + \cdots + G^q)\psi_0$, then we obtain the scattering amplitude in the p + q + n + 1 approximation. Actually,

$$D_n(\psi^{(p)}, \psi^{(q)}) = f_0 - \frac{k}{4\pi}(\psi_0, [(1 + G + \cdots$$

$$\cdots + G^p)(G^n - G^{n-1})(1 + G + \cdots + G^q) +$$

$$+ (1 + G + \cdots + G^p)G^{n-1} + G^{n-1}(1 + G + \cdots + G^q) +$$

$$+ (1 + G + \cdots + G^{n-2})]\psi_0). \tag{17}$$

The expression within the square brackets can easily be converted into the following form

$$G^{n-1}\left[\frac{G^{p+1} - 1}{G - 1}(G - 1)\frac{G^{q+1} - 1}{G - 1} + \frac{G^{p+1} - 1}{G - 1} + \frac{G^{q+1} - 1}{G - 1}\right] +$$

$$+ \frac{G^{n-1} - 1}{G - 1} = \frac{G^{p+q+n+1} - 1}{G - 1} = 1 + G + \cdots + G^{p+q+n}. \tag{18}$$

Thus,

$$D_n(\psi^{(p)}, \psi^{(q)}) = f_0 - \frac{k}{4\pi}(\psi_0, [1 + G + \cdots + G^{p+q+n}]\psi_0) =$$

$$= f_0 - \frac{k}{4\pi}(\psi^{(p+q+n)}, \psi_0) = f^{(p+q+n+1)} \tag{19}$$

according to formula (10.18). This same result can be obtained immediately from the variational principle, since during the computation of the variation of the functional D_n we have dropped only that term which contained the product of the variation φ_1 and φ_2. From this, in particular, it can be assumed that the functional $D_n(\varphi_2, \varphi_1)$ will give an accurate value for the scattering amplitude, if we substitute in it the accurate solution ψ only in place of one of the functions φ_2, φ_1, and the second remains arbitrary. Then we obtain /63

$$f = f_0 - \frac{k}{4\pi}\left[(\psi, G^n \varphi) - (\psi, G^{n-1}\varphi) + (\psi, G^{n-1}\psi_0) + \right.$$

$$\left. + (\psi_0, G^{n-1}\varphi) + (\psi_0, \psi_0) + \cdots + (\psi_0, G^{n-2}\psi_0)\right]. \qquad (20)$$

We will now mention the specifications which distinguish the function D_n obtained here from the Hulthen-Kohn functional which was explained in Chapter I.

First, the functionals D_n contain the Green function of the unexcited operator, and consequently their obvious form depends on how we break up the complete energy operator into excited and unexcited parts. If we assume that $V_0 = 0$ and $n = 1$, we obtain the Schwinger variational principle (Refs. 15, 16, 27, 42).

$$D_1(\varphi_2, \varphi_1) = \frac{k}{(4\pi)^2}\iint \varphi_2(\vec{r})\, V(\vec{r})\, \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \times$$

$$\times V(\vec{r}')\, \varphi_1(\vec{r}')\, d\tau\, d\tau' + \frac{1}{4\pi}\int \varphi_2(\vec{r})\, V(\vec{r})\, \varphi_1(\vec{r})\, d\tau -$$

$$- \frac{k}{4\pi}\int e^{ik\vec{v}_2\cdot\vec{r}}\, V(\vec{r})\, \varphi_1(\vec{r})\, d\tau - \frac{k}{4\pi}\int \varphi_2(\vec{r})\, V(\vec{r})\, e^{ik\vec{v}_1\cdot\vec{r}}\, d\tau;$$

$$f(\vec{v}_1, -\vec{v}_2) = \mathrm{St}\{D_1(\varphi_2, \varphi_1)\}. \qquad (21)$$

If we substitute the values $\varphi_1 = e^{ik\vec{v}_1\cdot\vec{r}}$, $\varphi_2 = e^{ik\vec{v}_2\cdot\vec{r}}$ in this functional, then we obtain an expression for the amplitude in the second Born approximation (2.27).

The second important characteristic of the investigated functional is contained in the fact that the functions, which are substituted in them, are not burdened by any particular limiting conditions, contrary to the Hulthen-Kohn functional where the functions had to contain at /64 infinity only plane and scattered waves. Here the sub-integral expression also contains, as multipliers, the functions (or operators) V of all arguments by which the integration was conducted, and thus the asymptotic form of the wave functions is unimportant. This makes it possible to use particularly simple test functions in the variational calculations and serves to simplify computation.

Furthermore, if the excitation V is a function, then during the calculation of D_n it is not necessary to differentiate the test functions. It is possible that this will be a definite advantage if the test functions are given in numerical form and the calculation is conducted on computers.

It should, however, be mentioned that even the simplest functional D_1 contains a dual integration of an entire space, and the functional D_n contains an $n + 1$ multiple integration. This circumstance complicates greatly the application of these functionals in numerical calculations.

We will establish a relation between the functionals D_n and the Kohn functional (6.17)*

$$J(\varphi_2, \varphi_1) = g_1(-\vec{v}_2) + \\ + \frac{k}{4\pi}\int \varphi_2 (\nabla^2 + k^2 - V_0 \cdot V)\,\varphi_1\, d\tau. \qquad (22)$$

First, we will present the function $g_1(-\vec{v}_2)$, which is included in this functional in the form of an integral. If we utilize Green's formula and transform the surface integral by the method examined in Section 6, then it is easy to obtain

$$\frac{k}{4\pi}\int [\psi_0(\vec{v}_2, \vec{r})\,\nabla^2\varphi_1 - \varphi_1\nabla^2\psi_0(\vec{v}_2, \vec{r})]\,d\tau = \\ = f_0(\vec{v}_1, -\vec{v}_2) - g_1(-\vec{v}_2). \qquad (23)$$

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*The relation between the Schwinger variational principle (21) and the Kohn variational principle was established by Kohn (Ref. 16).

from which

$$g_1(-\vec{v}_2) = f_0(\vec{v}_1, -\vec{v}_2) - \frac{k}{4\pi}\int [\psi_0(\vec{v}_2, \vec{r})(\nabla^2 + k^2 - V_0)\varphi_1 - \varphi_1(\nabla^2 + k^2 - V_0)\psi_0(\vec{v}_2, \vec{r})]\,d\tau =$$

$$= f_0(\vec{v}_1, -\vec{v}_2) - \frac{k}{4\pi}\int \psi_0(\vec{v}_2, \vec{r})(\nabla^2 + k^2 - V_0)\varphi_1\,d\tau. \qquad (24)$$

Thus, the functional (22) might be recorded in the following form [75]

$$J(\varphi_2, \varphi_1) = f_0(\vec{v}_1, -\vec{v}_2) - \frac{k}{4\pi}\left[\int \psi_0(\vec{v}_2, \vec{r})(\nabla^2 + k^2 - V_0)\varphi_1\,d\tau - \int \varphi_2(\nabla^2 + k^2 - V_0 - V)\varphi_1\,d\tau\right]. \qquad (25)$$

We will now consider the method of successive approximations, which is based on the integral equations (10.13) and (11.3), where in the capacity of a function in the null approximation we will use the arbitrary function φ. Then, after n-integrations

$$\varphi^{(n)} = \psi_0 + G\psi_0 + \cdots + G^n\varphi. \qquad (26)$$

We will notice that if φ is the accurate wave function ψ, then after any given number of iterations we will again obtain the same function. We will now prove that by substituting the function $\varphi^{(n)}$ in place of the function φ_1, in the functional J, we have the functional D_n. Actually,

$$\int \psi_0(\nabla^2 + k^2 - V_0)(\psi_0 + G\psi_0 + \cdots + G^{n-1}\psi_0 + G^n\varphi)\,d\tau -$$

$$- \int \varphi_2(\nabla^2 + k^2 - V_0 - V)(\psi_0 + G\psi_0 + \cdots + G^{n-1}\psi_0 +$$

$$+ G^n\varphi)\,d\tau = (\psi_0, \psi_0) + (\psi_0, G\psi_0) + \cdots + (\psi_0, G^{n-2}\psi_0) +$$

$$+ (\psi_0, G^{n-1}\varphi) - (\varphi_2, \psi_0) - (\varphi_2, G\psi_0) - \cdots - (\varphi_2, G^{n-2}\psi_0) -$$

$$- (\varphi_2, G^{n-1}\varphi) + (\varphi_2, \psi_0) + (\varphi_2, G\psi_0) + \cdots + (\varphi_2, G^{n-1}\psi_0) +$$

$$+ (\varphi_2, G^n\varphi) = (\varphi_2, G^n\varphi) - (\varphi_2, G^{n-1}\varphi) + (\varphi_2, G^{n-1}\psi_0) +$$

$$+ (\psi_0, G^{n-1} \varnothing) + (\psi_0, \psi_0) + (\psi_0, G\psi_0) + \cdots +$$

$$+ (\psi_0, G^{n-2} \psi_0). \tag{27}$$

Here the obvious equality was utilized

$$\int \varnothing_2 (\nabla^2 + k^2 - V_0) G^n \varnothing \, d\tau = (\varnothing_2, G^{n-1} \varnothing). \tag{28}$$

Thus, we actually have

$$J (\varnothing_2, \varnothing^{(n)}) = D_n (\varnothing_2, \varnothing). \tag{29}$$

It is not difficult to obtain an analogous formula /66

$$J (\varnothing^{(m)}, \varnothing_1) = D_m (\varnothing, \varnothing_1). \tag{30}$$

Actually,

$$\int \psi_0 (\nabla^2 + k^2 - V_0) \varnothing_1 \, d\tau - \int (\psi_0 + \psi_0 G + \cdots + \psi_0 G^{n-1} +$$

$$+ \varnothing G^n) (\nabla^2 + k^2 - V_0 - V) \varnothing_1 \, d\tau = (\psi_0 + \psi_0 G + \cdots$$

$$\cdots + \psi_0 G^{n-1} + \varnothing G^n, \varnothing_1) - \int (\psi_0 G + \cdots + \psi_0 G^{n-1} +$$

$$+ \varnothing G^n) (\nabla^2 + k^2 - V_0) [\psi_0 + (\varnothing_1 - \psi_0)] \, d\tau = (\psi_0 + \psi_0 G + \cdots$$

$$\cdots + \psi_0 G^{n-1} + \varnothing G^n, \varnothing_1) - (\psi_0 + \psi_0 G + \cdots + \psi_0 G^{n-2} +$$

$$+ \varnothing G^{n-1}, \varnothing_1 - \psi_0) = (\psi_0, \psi_0 + G\psi_0 + \cdots + G^{n-2} \psi_0) +$$

$$+ (\varnothing, G^n \varnothing_1) - (\varnothing, G^{n-1} \varnothing_1) + (\psi_0, G^{n-1} \varnothing_1) +$$

$$+ (\varnothing, G^{n-1} \psi_0). \tag{31}$$

It is also not difficult to derive the following formula

$$D_p\left(\varphi_2^{(m)}, \varphi_1^{(n)}\right) = D_{p+m+n}\left(\varphi_2, \varphi_1\right). \tag{32}$$

This formula contains formulas (29) and (30), if we assume that

$$D_0\left(\varphi_2, \varphi_1\right) = J\left(\varphi_2, \varphi_1\right). \tag{33}$$

Thus, we have acquired a succession of functionals which possess unique "group" properties (32). From among these only the Hulthen-Kohn functional D_0 does not depend on the specific selection of an unexcited operator. It can be seen from formula (32) that the functions φ_1 and φ_2 in the functionals D_1, D_2, $\cdots$ might have any given asymptotic form, since the interation process itself secures a correct asymptotic form for the function in the functional J.

The question arises as to which of the functionals D_n yields the better result if we conduct a direct variational calculation; that is, if we search for a stationary value of the functional in a certain collection of functions. This question is directly related to the problem of convergence of the method of successive approximations. Generally speaking, the iterative alogorithm converges for a broad class of /67 functions of the null approximation; however, cases when the first iterations "degrade" the function and give a less accurate result for the scattering amplitude are entirely possible. Thus, as a rule, by means of a direct calculation the functional D_n will give a more accurate result for the scattering amplitude the larger n is, if the class of the variated functions remains unchanged. Within this boundary

$$\lim_{n \to \infty} D_n\left(\varphi_2, \varphi_1\right) = f\left(\vec{v}_1, -\vec{v}_2\right), \tag{34}$$

whereby the function φ is practically unburdened by any conditions.

However, in particular the case of small n, a reverse case is entirely possible. It is well known that quite often the second approximation of the Born method yields a poorer result for the scattering amplitudes than the first approximation.

All results obtained here can be easily generalized to more complicated problems of scattering of electrons by atoms, and are thus more general.

§12. Direct Method of Phase Calculation Based on the Variational Principle (Reference 43)

The idea of approximate calculations based on the variational principle in collision theory is the same as in the case of problems of a discrete spectrum. This idea is contained in the fact that we attempt to satisfy the variational equations which were derived in the preceding chapter, not throughout the entire space of variated functions, but of a certain sub-space. During the selection of this sub-space (or class of variating functions) we have in mind, first of all, the physical considerations; that is, we strive for the functions to possess those properties of the desired wave function which are known to us beforehand. In addition, the selection of this class of functions is determined by practical considerations of the simplicity of calculation.

We will examine the simplest one dimensional equation /68

$$\left(\frac{d^2}{dr^2} + k^2 - V\right)\psi(r) = 0; \tag{1}$$

$$\psi(0) = 0, \tag{2}$$

$$\psi \sim A \sin(kr + \eta). \tag{3}$$

According to the formulas in Section 4, the variation of the functional

$$I(\psi) = \int_0^\infty \psi(r)\left(\frac{d^2}{dr^2} + k^2 - V\right)\psi(r)\,dr \tag{4}$$

equals

$$\delta I = -A^2 k \delta\eta. \tag{5}$$

By substituting in the functional (4) the function

$$\varphi(c_1, c_2, \cdots, c_n; \eta; r), \tag{6}$$

which satisfies the conditions of (2) and (3) at any given c_i, η. The normalizing coefficient A might, generally speaking, depend on the parameters c_i and η. By calculating the integral, we obtain a certain function of the parameters $c_1, \cdots, c_n, \eta$.

$$I(c_1, c_2, \cdots, c_n, \eta). \tag{7}$$

Thus, instead of a multitude of all functions which are continuous together with the first derivative and which satisfy the conditions of (2) and (3), we select a collection of functions (6) with arbitrary values of their parameters $c_1, \cdots, c_n, \eta$. The infinite dimensional Hilbert space functions are substituted with an $(n + 1)$-dimensional space function of the type (6).

By utilizing the variational principle (5), we may put down

$$\frac{\partial I}{\partial c_1} = 0, \quad \frac{\partial I}{\partial c_2} = 0, \quad \cdots, \quad \frac{\partial I}{\partial c_n} = 0; \quad \frac{\partial I}{\partial \eta} = -A^2 k. \tag{8}$$

In addition, generally speaking, there should be carried out the equation

$$I = 0, \tag{9}$$

which obviously follows from the stationarity of the functional in relation to the variation of the normalizing multiplier A.

For the purpose of determining $n + 1$ unknown $c_1, c_2, \cdots, c_n, \eta$ [1/69] we have $n + 2$ equations. Obviously it is impossible to generally satisfy these equations. Here, an essential difference between the variational methods and the discrete and solid spectra is apparent. In the case of a discrete spectrum the functional $\overline{E}$ contains a minimum for any given sub-multitude of normalized functions and by substitution in the integral of the $\overline{E}$ function which depends on the parameters c_i, these parameters were identically determined. Formula (5) should be fulfilled in any sub-multitude of functions which contains the accurate wave function ψ. However, the majority of functions determined by formula (6) never contained ψ in practice, and therefore the system of equations (8) may not be carried out for any of the functions in this sub-multitude.

In order to clarify the difference of what is obtained in the discrete and solid spectra, it is necessary to mention that the variational

principle (5) is not a stationarity condition (or minimum as is the case in a discrete spectrum) of a certain functional. The transition to a stationarity condition, as we have seen in Section 4, is not identical and is accompanied unavoidably by certain limitations, which are placed on the variation of the asymptotic form of the wave function. As soon as the transition is completed, the value of the parameters c_i and η are determined without difficulty; however, various means of transition are appropriate to various approximate methods and give, generally speaking, various values for the parameters c_i and η.

We will examine in detail the most simple, but extremely important case when a linear combination of the n-functions is substituted in a functional

$$\varphi = \sum_{i=1}^{n} c_i \varphi_i. \tag{10}$$

Let us assume that

$$\varphi_i(0) = 0 \qquad (i = 1, 2, \cdots, n); \tag{11}$$

$$\varphi_1 \sim \sin kr, \quad \varphi_2 \sim \cos kr;$$

$$\text{when } r \to \infty \ \varphi_j \to 0 \ (j = 3, 4, \cdots, n).$$

Then the functional (7) will be quadratic in c_i /70

$$I(\varphi) = \sum_{i,j=1}^{n} I_{ij} c_i c_j, \tag{12}$$

where

$$I_{ij} = \frac{1}{2}\left[\int_0^\infty \varphi_i \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi_j \, dr + \right.$$

$$\left. + \int_0^\infty \varphi_j \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi_i \, dr\right]. \tag{13}$$

By such a selection of a wave function the amplitude and phase are determined by the coefficients c_1, c_2. It is obvious that

$$c_1 = A \cos \eta, \quad c_2 = A \sin \eta, \tag{14}$$

$$A^2 \delta\eta = c_1 \delta c_2 - c_2 \delta c_1.$$

Thus, the variational principle (5) can be as follows:

$$\delta I = k \, (c_2 \delta c_1 - c_1 \delta c_2). \tag{15}$$

We will mention that the right hand part of this equation does not represent a complete differential, where the non-equivalence of this equation with respect to the stationarity condition follows.

Equation (8) for the determination of the coefficients $c_1, \cdots, c_n$ has, in this case, the following form (Ref. 39):

$$\sum_{j=1}^{n} I_{1j} c_j = \frac{k c_2}{2}; \quad \sum_{j=1}^{n} I_{2j} c_j = -\frac{k c_1}{2};$$

$$\sum_{j=1}^{n} I_{ij} c_j = 0 \quad (i = 3, 4, \cdots, n). \tag{16}$$

We have obtained a system n of homogeneous linear equations for the determination of n unknowns, $c_1, c_2, \cdots, c_n$. The condition for the presence of non-zero solutions to this system is

$$\begin{vmatrix} I_{11} & I_{12} - \frac{k}{2} & \cdots & I_{1n} \\ I_{21} + \frac{k}{2} & I_{22} & \cdots & I_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ I_{n1} & I_{n2} & \cdots & I_{nn} \end{vmatrix} = 0, \tag{17}$$

This condition, generally speaking, is not accomplished. By dropping /71 one of the equations (16) we construct a solvable system and we arrive at various formulations of the variational method. Acting in this manner we satisfy the general variational equation (5) in a certain (n - 1) space.

In the Kohn method (Ref. 16) the first of the equations cited here is dropped, and accordingly the coefficient c_1 does not variate and we may assume that $c_1 = 1$. Then

$$c_2 = \operatorname{tg} \eta, \quad \delta c_1 = 0, \quad \delta I = - k\delta c_2 = - k\delta (\operatorname{tg} \eta) \tag{18}$$

(Compare with formulas 4.22 and 4.23.)

In the Hulthen method (Ref. 11) the first two equations in the system (16) are dropped; however, the condition I = 0 is added. This is obtained if each of the equations (16) is multiplied by c_i and then combined. The condition I = 0 is derived from the stationarity J regarding the variational normalization of the multiplier. Such a variation is possible during the selection of a function of the form (10) and, accordingly, the condition I = 0 follows from equations (16). The condition I = 0 is quadratic in relation to the coefficients c_1 and c_2, and. accordingly, we obtain two solutions for the relation c_2/c_1.

In principle, other variational methods are also possible which correspond to dropping one of the consecutive equations in system (16); however, only the Hulthen-Kohn methods were in practical use until recently. Therefore, we will concern ourselves in more detail with these methods.

In the Kohn method we have, for the determination of the coefficients $c_2, \cdots, c_n$, the system of equations

$$\begin{aligned} &I_{21} + I_{22}c_2 + I_{23}c_3 + \cdots + I_{2n}c_n = - \frac{k}{2}, \\ &I_{31} + I_{32}c_2 + I_{33}c_3 + \cdots + I_{3n}c_n = 0, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &I_{n1} + I_{n2}c_2 + I_{n3}c_3 + \cdots + I_{nn}c_n = 0. \end{aligned} \tag{19}$$

By solving this system we find the approximate wave function $\tilde{\psi}$. Since the coefficient c_1 is fixed, we are not able to vary the normalizing coefficient freely, and consequently the value $I(\tilde{\psi})$ will be, generally speaking, /72

different from zero. This makes it possible to improve the value for tg η, by making use of formula (18) or (4.23). Thus, we obtain an approximate value for the tg η with the Kohn method

$$\operatorname{tg}\eta = c_2 + \frac{1}{k} I(\tilde{\psi}). \tag{20}$$

This formula can be transformed by utilizing the system (19). Actually

$$I(\tilde{\psi}) = \sum_{i=1}^{n} c_i (I_{i1}c_1 + I_{i2}c_2 + \cdots + I_{in}c_n) =$$

$$= c_1 (I_{11}c_1 + I_{12}c_2 + \cdots + I_{1n}c_n) - c_2 \cdot \frac{k}{2} =$$

$$= I_{11} + I_{12}c_2 + \cdots + I_{1n}c_n - \frac{k}{2} c_2. \tag{21}$$

Then formula (20) may have the following form

$$\operatorname{tg}\eta = I_{11} + \left(I_{12} + \frac{k}{2}\right) c_2 + I_{13}c_3 + \cdots + I_{1n}c_n. \tag{22}$$

Thus, in order to find a phase with the Kohn method it is necessary to first solve the system of equations (19) and then to substitute the coefficients obtained in the right hand part of formula (22). The coefficient c_2 by itself might give a considerably poorer value for tg η. In one of the first numerical calculations by Huang (Ref. 20) on the scattering of particles by a force field with a Yukawa potential $Ae^{-\alpha r}/r$ this circumstance was not taken into consideration and its result differed from those of other calculations by a considerable degree. After modification of the Huang results according to formula (22), which was done by Hulthen and Olsson (Ref. 44), complete agreement with the preceding calculations was obtained.

In the Hulthen method the condition $I(\tilde{\psi}) = 0$ was carried out beforehand; consequently, the value of the phase $\tilde{\eta}$, which was obtained from the asymptotic form $\tilde{\varphi}$, differed in magnitude from the accurate value of the phase by $(\varepsilon\psi)^2$, and within the frameworks of this approximation this value cannot be defined more accurately From this standpoint the Hulthen /73 method is more "consistent" than the other methods. The results of numerical calculations indicate that the Hulthen method also normally leads to better results than the Kohn method.

In order to establish a relation between the Hulthen and Kohn methods we will return to the system of equations (16), and by utilizing the last $n - 2$ equations, which should be carried out in both methods, we will eliminate $c_3, c_4, \cdots, c_n$. Then we obtain a system of two equations for c_1 and c_2

$$A_{11}c_1 + A_{12}c_2 = \frac{k}{2}c_2,$$

$$A_{21}c_1 + A_{22}c_2 = -\frac{k}{2}c_1. \tag{23}$$

By multiplying the first equation by c_1, the second by c_2, and by combining them, we obtain the Hulthen equation

$$I = A_{11}c_1^2 + 2A_{12}c_1c_2 + A_{22}c_2^2 = 0. \tag{24}$$

From this we obtain with the Hulthen method for the desired value $x = \frac{c_2}{c_1} = \operatorname{tg}\eta$

$$x = \frac{1}{A_{22}}\left(-A_{12} \pm \sqrt{A_{12}^2 - A_{11}A_{22}}\right). \tag{25}$$

With the Kohn method, we obtain analogously

$$c_2 = -\frac{1}{A_{22}}\left(A_{21} + \frac{k}{2}\right),$$

$$x = c_2 + \frac{1}{k}I = c_2 + \frac{1}{k}\left(A_{22}c_2^2 + 2A_{12}c_2 + A_{11}\right) =$$

$$= \frac{1}{A_{22}}\left(-A_{12} - \frac{k}{2}\right) + \frac{1}{kA_{22}}\left(A_{11}A_{22} - A_{12}^2 + \frac{k^2}{4}\right). \tag{26}$$

It is obvious that the results obtained with the Hulthen and Kohn methods should be relatively close if only the original functions φ_i are selected satisfactorily.

Results obtained with both methods will coincide if only equations (23) are common; that is, if the following equation is true /74

$$\begin{vmatrix} A_{11} & A_{12} - \frac{k}{2} \\ A_{21} + \frac{k}{2} & A_{22} \end{vmatrix} = 0,$$

$$A_{12}^2 - A_{11}A_{22} = \frac{k^2}{4}, \tag{27}$$

which obviously equals equation (17).

It can be easily seen that if we use the symbol -, in formula (25), formulas (25) and (26) will actually coincide when we carry out the conditions of (27). Thus, during the calculation with the Hulthen method it is not necessary (as was shown, for instance, in Refs. 11, 20, 21) to compare the results obtained with the results of other approximate calculations, in order to select the true root from two possible roots. Only one symbol in formula (25) -- the minus symbol -- has any physical sense. In addition, the condition (27) provides a sufficiently reliable criterion for the quality of the selected wave function. Thus, it can be seen why, if only the function is selected satisfactorily, the Hulthen method should not yield any complex values for the phase tangent. Actually the sub-radical expression in this case is close to the value $k^2/4$, and thus it is positive.

In order to understand the formal nature of the second solution in the Hulthen method, we will mention that if condition (27) is carried out, then the second radical will equal

$$x' = \frac{1}{A_{22}}\left(-A_{12} + \frac{k}{2}\right). \tag{28}$$

This same result will be obtained from formula (26), if we would formally change in it k by -k, leaving the coefficients A_{ij} without any changes. Returning to the original formulation of the variational principle, we can see that the second radical from the phase tangent is obtained /75 from the formal attempts to satisfy in the area of the function (10) the variational equality

$$\delta I = -k\,(c_2\delta c_1 - c_1\delta c_2) = A^2 k\delta\eta, \tag{29}$$

which is obtained from the original variational principle (15) by changing the symbol in the right hand part.

It is obvious, however, that the equality (29) makes no sense. Actually the wave function is already simply determined from the stationarity requirements of the functional I regarding the variations which die out at infinity. It follows from this fact that the result, which was obtained in the case of δI during the variation of the asymptotic function, is obtained identically and can not be arbitrarily changed. Consequently, equation (29) does not determine any functions in general. If we solved the problem by using the Hulthen method, increasing regularly the number of variated functions n, then the second radical (the symbol + in the formula 25) would either not converge at all toward a determined limit, or this limit would essentially depend on the selection of succession on the part of the function φ_i. Numerical calculations confirm this assertion.

We will now investigate the question on the degree to which the integral identity which, (as shown in Section 10) is also derived from the variational principle, should be carried out in the case of the obtained approximate function. In the given simplest case this identity has the following form*

$$\operatorname{tg}\eta = \frac{1}{k}\int_0^\infty \psi\left(\frac{d^2}{dr^2} + k^2 - V\right)\sin kr\, dr =$$

$$= -\frac{1}{k}\int_0^\infty \sin kr \cdot V\psi\, dr. \qquad (30)$$

We will assume that the function $\varphi_1 = \sin kr$. Such a selection of the function φ_1 is most simple and practical and is the most frequently used method. We will substitute in formula (30), in place of the accurate /76 wave function ψ its approximate expression (10). Then we obtain

$$\operatorname{tg}\eta = \frac{1}{k}\sum_{i=1}^{n} c_i \int_0^\infty \varphi_i\left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi_1 dr =$$

$$= \frac{1}{k}\sum_{i=1}^{n} I_{1i}c_i + \frac{1}{2}c_2. \qquad (31)$$

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*It is assumed here that the accurate wave function ψ has this asymptotic form: $\psi \sim \sin kr + \operatorname{tg}\eta \cdot \cos kr$.

During the derivation of this formula equalities were utilized as a result of formulae (11) and (13)

$$I_{1i} = \int_0^\infty \varphi_1 \left(\frac{d^2}{dr^2} + k^2 - V \right) \varphi_i dr \quad (i = 3, 4, \ldots, n);$$

$$I_{12} = \int \varphi_2 \left(\frac{d^2}{dr^2} + k^2 - V \right) \varphi_1 dr + \frac{k}{2} . \tag{32}$$

Formula (31) coincides with formula (22) and, thus, during the phase calculation with the Kohn method, the integral identity is automatically carried out.

On the other hand, if in the left hand part of formula (31) we substitute in place of tg η the coefficient c_2, then we obtain the first equation of the system (16). From this it can be assumed that, if during a calculation with the Hulthen method, the integral identity is carried out, the system of equations (16) is self consistent and the determinant (17) equals zero; thus, the Hulthen method, as well as the Kohn method, yields identical results. This proof of the integral identity is equivalent to a direct comparison of the phase calculation results by the Hulthen and Kohn methods; therefore, it does not represent any independent criteria which would confirm the accuracy of the variational calculation.

The selection of variating functions plays an important role during the calculation with the variational methods. At the present time in the majority of variational calculations the wave function for scattering /77 was sought in the form

$$\psi = \sin kr + u(r) \cos kr, \tag{33}$$

where u(r) is a certain function which contains variating parameters which, in turn, satisfy the condition u(0) = 0 and are finite when $r \to \infty$. It is obvious that $\lim_{r\to\infty} u(r) = \operatorname{tg} \eta$. The variational principle can be formulated directly for the function u(r), as was done by I. E. Tamm (Ref. 13). However, such a selection of a wave function should not be considered entirely satisfactory. V. A. Fok (Ref. 14) has proven that, in the case of an accurate wave function ψ, the function u(r) will go to infinity at the points $r = (n + 1/2)\frac{\pi}{k}$ $(n = 0, 1, \ldots)$.

It is clear that, when determining such a function with a variational method, we cannot anticipate beforehand satisfactory results.*

The selection of a wave function in the formula (33) can be examined from another standpoint, considering that a variational calculation at additional conditions which were placed on the wave functions were conducted.

$$\psi\left(\frac{n\pi}{k}+\frac{\pi}{2k}\right)=(-)^n \qquad (n=1,\ 2,\ \cdots). \tag{34}$$

Outside of the radius of action of the forces ($r > a$) this condition is carried out rigorously; however, when $r < a$ this condition has no basis at all.

Nevertheless, the results of variational calculations, which were conducted with the functions of the form (33), agree in a number of cases with the results of calculations which were conducted by other methods. This circumstance is possibly related to the fact that the local conditions (34) which were placed on the function ψ (the value of ψ is fixed at certain values of r) has a comparatively slow effect on the result /78 of the variational calculation as opposed to the integral conditions (for instance, the orthogonality toward wave functions of the basic state during a variational calculation of the excited related states).

If we use the Schwinger variational principle in the capacity of a foundation for calculations, then the corresponding direct method can be easily formulated and the non-identical selection of a method, which was discussed above, does not occur. This is related to the fact that the variation of the wave functions and the stationary expression for a phase might be arbitrary and the asymptotic form of the variated functions cannot be fixed. In connection with this a number of attempts were made to apply the Schwinger method toward the solution of physical problems (Refs. 42, 45, 46, 47). However, the results obtained are still not sufficiently reliable and the presence of a double integration makes the calculation quite cumbersome.

The direct method of the collision theory can not only be applied for phase calculations, but also directly for calculations of the scattering amplitude. There are available, at the present time, several calculations of such a type (Refs. 42, 45, 48); however, their accuracy

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*The indicated difficulty is treated in Refs. 14 and 19. The wave function ψ is determined in these works by two material (or one complex) functions, for the determination of which the variational principle was formulated.

is insufficient and the problem of selection of such test functions which would enable a sufficiently simple and reliable calculation remains open. We will also mention that the variational calculation of the scattering amplitude by a zero-angle yields the possibility of obtaining the value of the complete effect of cross-section. This method is discussed in Refs. 42 and 46.

§13. The Variational Principle and the Method of a Self-Adjusted Field

The equations of a self-adjusted field for a wave function of a multi-electron system in a combined state is derived most naturally from the variational principle, as was shown in the works by V. A. Fok (Ref. 9). Since then, similar equations for problems on the scattering of electrons by an atom have been derived without application of the variational principle until the present time. The usual method for obtaining these equations is contained in the fact that the wave function is presented/79 in the following form

$$\Psi = \sum_n \psi_n F_n, \tag{1}$$

where ψ_n is the wave function of the atom and F_n are the functions which characterize the bombarding and scattered electrons. In case of an exchange calculation this sum should properly be symmetrized. Furthermore, from the entire sum there remains only one term (or several terms) which correspond to the method of configuration superposition for a discrete spectrum. If the expression obtained is substituted in the equation, it is multiplied on the left hand side by the wave function of the atom and integrated over the coordinates of the atomic electrons. In a very simple case this derivative was given in Section 1. However, such a method for obtaining an equation for the function F requires additional substantiation. It is not at all obvious beforehand why equation (1.1) should be multiplied by the wave function of the atom. Generally speaking, we could have multiplied this equation by any given function of the coordinates of the bombarding and atomic electrons and, after integration over the coordinates of atomic electrons, we would have obtained various equations for the function F. If the expression (1.7) for the wave function had been accurate, then all these equations would have been satisfied. On the other hand, if expression (1.7) is approximate then, generally speaking, it is not clear which of these equations is the best and in what sense.

Therefore, during the derivation of approximate equations for the wave functions it is advantageous to do it on the basis of the variational principle.* For the sake of simplicity we will examine here only a case of electron scattering by hydrogen, disregarding, as usual, that part of the solution which contains the functions of the solid spectra. We will stop at the characteristics which occur during the examination of problems of scattering of electrons by more complicated atoms.

The wave function of the hydrogen atom will be recorded as /80

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \sum_i \psi_i [(\vec{r}_1) F_i (\vec{r}_2) \pm \psi_i (\vec{r}_2) F_i (\vec{r}_1)] \qquad (2)$$

where ψ_i satisfy equations (8.2). We will consider the stationarity condition of the functional

$$I = \frac{1}{2} \iint \sum_i [\psi_i (\vec{r}_1) F_i^{in} (\vec{r}_2) \pm \psi_i (\vec{r}_2) F_i^{in} (\vec{r}_1)]^* \times$$

$$\times L \sum_j [\psi_j (\vec{r}_1) F_j^{out} (\vec{r}_2) \pm \psi_j (\vec{r}_2) F_j^{out} (\vec{r}_1)] \, d\tau_1 d\tau_2, \qquad (3)$$

where the symbols "out" and "in" indicate that in the asymptotic form of the function F_i there might be present only plane or divergent waves, or convergent waves with the operator L as determined by equation (7.1).

In order to obtain the equations for the function F_i we might limit ourselves only to such variations of δF_i which do not change the asymptotic form of the wave function. It was already indicated in Section 8 that the functional I is stationary in relation to these variations.

We will introduce the following definitions

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*This circumstance was pointed out in the work by V. I. Ochkur and Yu. V. Petrov (Ref. 49).

$$H_{ij}(\vec{r}_2) = \int \psi_i^*(\vec{r}_1)\, L\psi_j(\vec{r}_1)\, d\tau_1 =$$

$$= \int \psi_i^*(r_1)\left(\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}} + 2E\right)\psi_j(\vec{r}_1)\, d\tau_1 =$$

$$= \delta_{ij}\left(\nabla_2^2 + \frac{2}{r_2} + 2E - 2E_i\right) + (-2)\int \frac{\psi_i(r_1)\,\psi_j(r_1)}{r_{12}}\, d\tau_1 =$$

$$= \delta_{ij}\left(\nabla_2^2 + \frac{2}{r_2} + k_i^2\right) + V_{ij}(\vec{r}_2); \qquad (4)$$

$$K_{ij}(\vec{r}_1, \vec{r}_2) = \psi_i^*(\vec{r}_1)\, L\psi_j(\vec{r}_2) =$$

$$= \psi_i^*(\vec{r}_1)\left(2E - 2E_i - 2E_j - \frac{2}{r_{12}}\right)\psi_j(\vec{r}_2); \qquad (5)$$

$$V_{ij}(\vec{r}_2) = (-2)\int \frac{\psi_i^*(\vec{r}_1)\,\psi_j(\vec{r}_1)}{r_{12}}\, d\tau_1 . \qquad (6)$$

(In formula (5) we have operated on the function ψ_i on the right hand /81 side with a part of the operator L.) The functional I may be as follows

$$I = \sum_{i,j}\left[\int F_i^{in*}(\vec{r})\, H_{ij}(\vec{r})\, F_j^{out}(\vec{r})\, d\tau \pm \right.$$

$$\left. \pm \iint F_i^{in*}(\vec{r})\, K_{ij}(\vec{r}, \vec{r}')\, F_j^{out}(\vec{r}')\, d\tau\, d\tau'\right]. \qquad (7)$$

From the condition of stationarity of this functional in relation to the arbitrary variations of the functions F_i^{in}, F_j^{out}, we directly obtain a system of equations for these functions. Therefore, F_i^{in} and F_j^{out} yield the identical equations

$$\sum_i H_{ij}(\vec{r})\, F_j(\vec{r}) \pm \sum_j \int K_{ij}(\vec{r}, \vec{r}')\, F_i(\vec{r}')\, d\tau' = 0. \qquad (8)$$

This system may be recorded as follows

$$\left(\nabla^2 + k_i^2 + \frac{2}{r}\right) F_i(\vec{r}) + \sum_j [V_{ij}(\vec{r}) F_j(\vec{r}) \pm$$

$$\pm \int K_{ij}(\vec{r}, \vec{r}') F_j(\vec{r}') d\tau'] = 0. \qquad (9)$$

If we consider, in the formula (1) and henceforth, that the summarization is conducted in all states including the solid spectrum, then the system obtained will be accurate. On the other hand, if we could state the final number of terms in the row then, as can be seen from the conclusion, the solution to the system (9) will yield a single function ψ, which satisfies the variational principle in the class of the function (1) with an arbitrary F_i. In that sense the function obtained will be optimum in its class.

We will examine an important specific case when we limit ourselves to only one of the i^{th} cerms of the sum (1). Then, in the case of the function F_i, we obtain the equation

$$\left(\nabla^2 + k_i^2 + \frac{2}{r}\right) F_i(\vec{r}) + V_{ii}(\vec{r}) F_i(\vec{r}) \pm$$

$$\pm \int K_{ii}(\vec{r}, \vec{r}') F_i(\vec{r}') d\tau' = 0; \qquad (10)$$

from the solution of which we obtain the wave function /82

$$\psi_{\pm}^{(i)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \psi_i[(\vec{r}_1) F_i(\vec{r}_2) \pm \psi_i(\vec{r}_2) F_1(\vec{r}_1)]. \qquad (11)$$

This function satisfies the variational principle in the class of functions of type (11) with an arbitrary F_i. Such an approximate method, according to the analogy with problems of a discrete spectrum, is called the Fok method or the method of a self-adjusted field with an exchange. In the case of large r_1 and r_2 in the asymptotic solution of function (9), only an elastically scattered wave will remain in addition to the incident wave. Therefore, by considering only the wave function (11), which was calculated by the Fok method, we can take into consideration only the elastic collisions and disregard all inelastic processes. However, in spite of such seemingly rough approximation, the Fok method gives good results in many cases. It can be assumed that from the condition of the

unitarity of the scattering matrix, that part of the elastic collisions in the complete effective cross section normally represents not less than one half (Chapter III). This consideration might serve as an argument in favor of the Fok method.

If we investigate the problem of scattering of electrons by more complicated atoms, then we should mention, first of all, that the atomic wave functions are known only approximately. This difficulty was considered in Section 8 and we will not concern ourselves with it at this point. From results obtained in Section 8 it is obvious that if the wave function is represented in the form $F\Phi$, where F is the function of bombarding electrons and Φ is the function of the atomic electron, then it is impossible to calculate the effects of the bombarding electron and the atomic polarization function Φ consecutively, since this function should, in turn, satisfy the variational principle in a certain class of functions, and consequently it is calculated independently of the form F.

In this manner the method of a self-adjusted field for problems of scattering possess a characteristic distinction from this same method for related states. The bombarding electron does not affect the motion of the atomic electrons within the framework of this approximation. This characteristic facilitates the proper calculations, since instead of /83 solving the joint n + 1 system of equations, it remains for us only to solve one equation for the function of the bombarding electron. The calculation of a wave function of the atom can be conducted independently or by way of utilizing the already available results of approximate calculations by these methods which are based in one way or another on the variational principle (for instance, with the method of a self-adjusted field). The effect of a bombarding electron on atomic electrons (that is, the polarization effect) can be calculated either with the method of configuration superposition, or by introducing a clear dependence of the wave function on the distance between the bombarding and atomic electrons.

When we pass on to multi-electron problems the method of symmetrization of the coordinate wave of the function becomes essentially more complicated. If S is the complete spin of the atom which is bombarded by an electron, then the spin of the total system might equal either S + 1/2, or S - 1/2. The electrons in an atom might be divided into two groups ($\frac{n}{2}$ + S and $\frac{n}{2}$ - S), whereby the wave function of the atom is antisymmetric in relation to the shift of coordinates inside of each group. In addition there should be carried out the Fok condition of cyclic symmetry (Ref. 50). If the spin of the total system equals S + 1/2, then the bombarding electron joins a large group of electrons, and symmetrization is conducted very simply. The second case, when the

bombarding electron joins a smaller group, is more complicated. The problems of symmetrization of a coordinate wave function were investigated in detail in the work by G. F. Drukarev (Ref. 51).

We will discuss here only the final results for collisions with helium, that is, for the case of three electrons. Here the spin of an atom might equal either zero, in which case the wave function ψ is symmetrical: $\psi_0(\vec{r}_1, \vec{r}_2) = \psi_0(\vec{r}_2, \vec{r}_1)$, or it might equal a unit, in which case the coordinate function ψ is antisymmetric: $\psi_1(\vec{r}_1, \vec{r}_2) = -\psi_1(\vec{r}_2, \vec{r}_1)$. In the first case we can construct only one function with S = 1/2:

$$\Psi_{1/2}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = F(\vec{r}_1)\,\psi_0(\vec{r}_2, \vec{r}_3) - F(\vec{r}_2)\,\psi_0(\vec{r}_1, \vec{r}_3). \quad (12)$$

In the second case the spin S might equal 1/2 and 3/2; /84

$$\Psi_{1/2} = 2F(\vec{r}_1)\,\psi_1(\vec{r}_2, \vec{r}_3) + F(\vec{r}_2)\,\psi_1(\vec{r}_1, \vec{r}_3) + F(\vec{r}_3)\,\psi_1(\vec{r}_2, \vec{r}_1), \quad (13)$$

$$\Psi_{3/2} = F(\vec{r}_1)\,\psi_1(\vec{r}_2, \vec{r}_3) + F(\vec{r}_2)\,\psi_1(\vec{r}_3, \vec{r}_1) + F(\vec{r}_3)\,\psi_1(\vec{r}_1, \vec{r}_2). \quad (14)$$

By substituting the obtained functions in the functional and by requiring its stationarity, it is easy to obtain the proper integral differential equations for the function F. After solving these equations it is possible to obtain the approximate wave function for the scattering of the electron by an atom which is in a ground as well as excited state.

The numerical solution to the equation of the self-adjusted field is possible only after a resolution of the function F by the partial waves. However, even after that, if we take into consideration the exchange, it is still sufficiently difficult to solve the proper integral differential equation.

A numerical calculation of this type was conducted by Morse and Allis (Ref. 3) for the case of collisions of electrons with hydrogen (ℓ = 0, 1); however, in the case of S = 0 the accuracy of this calculation is obviously insufficient (Ref. 75). It is possible, however, to take a different approach to this problem and calculate the function F (or the corresponding partial waves) with the help of direct methods,

that is, based directly on the functional (7) or analogous functions for more complex problems. This type of calculation was recently conducted for collisions of electrons with hydrogen (Refs. 21, 22), hydrogen type ions (Ref. 23) and, finally, collisions with helium (Refs. 24, 25) for the basic and primarily excited states.

§14. The Variational Principle and the Classification of Approximate Methods for the Calculation of Inelastic Collisions /85

We have mentioned already in the preceding section that the wave functions which were calculated with the method of a self-adjusted field contain only elastically scattered waves at large distances from the scatterer.

However, we are still able to calculate the amplitude of inelastic scattering with the help of these approximate functions, if we assume that these functions do not differ strongly from the accurate wave functions; that is, that the inelastic scattering is sufficiently slow in comparison with the elastic scatterings. In that case we may substitute the approximate function of a self-adjusted field in the expression for the amplitude of inelastic scattering, which is stationary in regard to slow variations of accurate wave functions (derived in Section 8). For scattering on a hydrogen atom this stationary expression has the form

$$f_{ij}(\vec{v}_1, -\vec{v}_2) = \\ = \mathrm{St}\left\{\tilde{f}_{ij}(\vec{v}_1, -\vec{v}_2) + \frac{k_i}{4\pi}\iint \tilde{\Psi}_2^{(j)} L\Psi_1^{(} \, d\tau_1 \, d\tau_2\right\}. \tag{1}$$

After substituting in this expression for the wave functions

$$\tilde{\Psi}_1^{(i)} = \frac{1}{\sqrt{2}}\left[F_i^{\mathrm{out}}(\vec{r}_1)\,\psi_i(\vec{r}_2) \pm F_i^{\mathrm{out}}(\vec{r}_2)\,\psi_i(\vec{r}_1)\right],$$

$$\tilde{\Psi}^{(j)} = \frac{1}{\sqrt{2}}\left[F_j^{\mathrm{in}}(\vec{r}_1)\,\psi_j(\vec{r}_2) \pm F_j^{\mathrm{in}}(\vec{r}_2)\,\psi_j(\vec{r}_1)\right]^*, \tag{2}$$

we can use formula (13.7) taking from it the term with a single value of i and j. The quantity $\tilde{f}_{ij}$ is, in this case, equal to zero, and we obtain the approximation

$$f_{ij}(\vec{v}_1, -\vec{v}_2) = \frac{k_j}{4\pi}\left[\int F_j^{in*}(\vec{r})\, V_{ij}(\vec{r})\, F^{out}(\vec{r})\, d\tau \pm \right.$$

$$\left. \pm \iint F^{in*}(\vec{r})\, K_{ij}(\vec{r}, \vec{r}')\, F_i^{out}(\vec{r}')\, d\tau\, d\tau'\right]. \qquad (3)$$

The acquired result coincides with the one obtained for the /86 inelastic scattering by the method of excitation. (See Mott and Massey, Ref. 1, p. 180.) That method is usually derived by analyzing a system (13.9). If we keep in the expression for the wave function only two terms, the i term and the j term, we obtain a system of two equations for the functions F_i and F_j:

$$(\nabla^2 + k_i^2) F_i + U_{ii}F_i \pm \int K_{ii}(\vec{r}, \vec{r}') F_i(\vec{r}')\, d\tau' =$$

$$= -U_{ij}F_j \mp \int K_{ij}(\vec{r}, \vec{r}') F_j(\vec{r}')\, d\tau',$$

$$(\nabla^2 + k_j^2) F_j + U_{jj}F_j \pm \int K_{jj}(\vec{r}, \vec{r}') F_j(\vec{r}')\, d\tau' =$$

$$= -U_{ji}F_i \mp \int K_{ji}(\vec{r}, \vec{r}') F_j(\vec{r}')\, d\tau'; \qquad (4)$$

$$U_{ij} = V_{ij} + \frac{2}{r}\delta_{ij}.$$

This system of equations can be solved by the method of successive approaches. For that we equate the right sides of first and second equations to zero and find the solutions for the two equations for the zero approximation $F_i^{(0)}$ and $F_j^{(0)}$, which corresponds to the method of self-adjusted field, fiscussed in the preceding paragraph. Then we substitute the obtained solution in the right sides of both equations and, solving them, obtain functions $F_i^{(1)}$ and $F_j^{(1)}$ in the first approximation. In article (53) it was shown that the amplitude of scattering in function $F_j^{(1)}$ is determined by formula (3); that is, for the determination of the asymptotic form of function $F_j^{(1)}$ it is sufficient to know only $F_i^{(0)}$ and $F_j^{(0)}$.

It is obvious that formula (1) could also be utilized for refining the expression for the amplitude of elastic scattering f_{ii}, if the corresponding equation (13.10) is being solved by approximation so that the functional $\iint \Psi_2^{(i)} L\Psi_1^{(i)}\, d\tau_1\, d\tau_2$ is not equal to zero.

The formulae presented here could be readily rewritten for /87
spearate partial waves.

Thus, from the standpoint of the variational principle, we are reaching a distinct classification of the approximate calculation method for elastic and inelastic collisions, depending on the various functions being substituted in the right side of the linear function (1).

In his review of calculations of collisions of slow electrons with atoms, Massey (Ref. 52) gives a classification of approximate calculation methods for inelastic collisions, based on dropping some terms of system (4), taking full account of the others, and accounting only in first approximation for the benefit of some which are considered small. Table 1 is given in that review. (We have somewhat modified the designations of the methods.)

TABLE 1

Dropped	Considered Small	Not Considered Small	Designation of Method
U_{11}, U_{22} K_{11}, K_{12}, K_{22}	U_{12}	---	Born's
U_{11}, U_{22} K_{11}, K_{22}	U_{12}, K_{12}	---	Born-Oppenheimer
K_{11}, K_{12}, K_{22}	U_{12}	U_{11}, U_{22}	Excitation waves
K_{11}, K_{22}	U_{12}, K_{12}	U_{11}, U_{22}	Excitation waves with symmetrization
---	U_{12}, K_{12}	U_{11}, U_{22} K_{11}, K_{22}	Excitation waves with symmetrization and exchange
K_{11}, K_{12}, K_{22}	---	U_{11}, U_{12}, U_{22}	Strong bond
---	---	All	Strong bond with exchange and symmetrization

Examining the same methods from the variational standpoint, we /88 obtain Table 2.

TABLE 2

Method	Forms of Wave Functions to be Inserted in the Functional
Born's	$e^{i\vec{k}\cdot\vec{r}_1}\,\psi(\vec{r}_2)$
Born-Oppenheimer	$e^{i\vec{k}\cdot\vec{r}_1}\,\psi(\vec{r}_2) \pm e^{i\vec{k}\cdot\vec{r}_2}\,\psi(\vec{r}_1)$
Excitation waves	$F(\vec{r}_1)\,\psi(\vec{r}_2)$
Excitation waves with symmetrization	$F(\vec{r}_1)\,\psi(\vec{r}_2) \pm F(\vec{r}_2)\,\psi(\vec{r}_1)$
Excitation waves with symmetrization and exchange	$F^{\pm}(\vec{r}_1)\,\psi(\vec{r}_2) \pm F^{\pm}(\vec{r}_2)\,\psi(\vec{r}_1)$
Strong bond	$F_1(\vec{r}_1)\,\psi_1(\vec{r}_2) + F_2(\vec{r}_1)\,\psi_2(\vec{r}_2)$
Strong bond with symmetrization	$F_1^{\pm}(\vec{r}_1)\,\psi_1(\vec{r}_2) + F_2^{\pm}(\vec{r}_1)\,\psi_2(\vec{r}_2) \pm$ $\pm F_1^{\pm}(\vec{r}_2)\,\psi_1(\vec{r}_1) \pm F_2^{\pm}(\vec{r}_2)\,\psi_2(\vec{r}_1)$

Here ψ equals the respective atomic wave functions, while functions F, in turn, are determined from the conditions making the functional stationary in the respective classes of the functions. The classes are determined from Table 3.

TABLE 3

Function	Class of Functions in Which the Functional is Stationary
F	$\Phi(\vec{r}_1)\,\Psi(\vec{r}_2)$
$F^{\mp}$	$\Phi(\vec{r}_1)\,\Psi(\vec{r}_2) \mp \Phi(\vec{r}_2)\,\Psi(\vec{r}_1)$
F_1, F_2	$\Phi_1(\vec{r}_1)\,\Psi_1(\vec{r}_2) + \Phi_2(\vec{r}_1)\,\Psi_2(\vec{r}_2)$
$F_i^{\pm}, F_2^{\pm}$	$\Phi_1(\vec{r}_1)\,\Psi_1(\vec{r}_2) + \Phi_2(\vec{r}_1)\,\Psi_2(\vec{r}_2) \pm \Phi_1(\vec{r}_2)\,\Psi_1(\vec{r}_1) \pm \pm \Phi_2(\vec{r}_2)\,\Psi_2(\vec{r}_1)$

Here, $\Phi(\vec{r})$ equals arbitrary functions of the character necessary for asymptotic behavior (i.e., having at large r the form of a plane /89 wave of given direction and convergent or divergent spherical wave with arbitrary amplitude, depending on the problem being solved and on where the given function is being inserted).

Thus, the variational principle, while not leading in this case to new equations or new methods, enables us to substantiate more emphatically the old methods and to examine them from a new viewpoint.

Computations (by the method of excitation waves with consideration of exchange and symmetrization) of excitation by electronic impingement of atoms of hydrogen (Ref. 22), helium (Ref. 25) and of an ion He^+ (Ref. 23) are presently available. These computations contained the solutions of equations of the self-adjusted field obtained with the help of direct variational methods mentioned at the end of the preceding paragraph.

These computations made it possible to explain the resonant character of behavior of the effective section near the threshold and to obtain results in satisfactory agreement with experiments where experimental data is available (excitation of helium).

§15. Variational Computations of Elastic Collisions of Electrons with Hydrogen

A detailed survey of variational computations of collisions between slow electrons and atoms, as well as a comparison with other computations, is to be found in a reviewing article by Massey (Ref. 52), now being translated into Russian, and in a review by G. F. Drukarev (Ref. 54).

We will concentrate here on the computation of elastic collisions of electrons with hydrogen atoms carried out by Massey and Moiseiwitsch (Ref. 21), i.e., on the simplest problem utilized throughout the book for demonstrating the application of variational methods to the problem of multi-body collisions. This problem is now the only one for which it was possible to perform a variational computation with consideration of polarization; i.e., it was possible manifestly to introduce in the wave function the distance between electrons r_{12} and to step beyond the borders of the self-adjustment method. The equation of self-adjusted field /90 for s- and p-scatterings was numerically integrated in the paper of Macdougall (Ref. 55) without consideration of exchange, and in the paper of Morse and Allis with consideration of exchange. In the latter case, for the solving of the equations, use was made of the Busch differential analyzer -- a mechanical calculator of the continuous action type. Only the s-scattering was analyzed in the work of Massey and Moiseiwitsch; the variable functions were selected in the forms:

$$\Psi_1 = \frac{1}{\sqrt{\pi}} e^{-r_1} \left[\frac{\sin kr_2}{kr_2} + (a + be^{-r_2})(1 - e^{-r_2}) \frac{\cos kr_2}{kr_2}\right], \tag{1}$$

$$\Psi_2 = \frac{1}{\sqrt{2}} [\Psi_1(r_1, r_2) \pm \Psi_1(r_2, r_1)], \tag{2}$$

$$\Psi_3 = \frac{1}{\sqrt{\pi}} e^{-r_1} \left\{\frac{\sin kr_2}{kr_2} + \right.$$

$$\left. + [a + (b + cr_{12}) e^{-r_2}](1 - e^{-r_2}) \frac{\cos kr_2}{kr_2}\right\}, \tag{3}$$

$$\Psi_4 = \frac{1}{\sqrt{2}} [\Psi_3(r_1, r_2) \pm \Psi_3(r_2, r_1)]. \tag{4}$$

Here a, b, c are variable parameters, $a = \operatorname{tg} \eta$ determining the phase of wave functions.

The results of the various computations are presented in Fig. 1. Obviously the variational computations with function Ψ_1 should be compared with the numerical solution of the Hartree equation, while the variational computation with the function Ψ_2 should be compared with the numerical solution of the Fok equations.

The variational computations with function Ψ_4 should, generally speaking, furnish the most reliable results; however, owing to the absence of experimental data, a comparison can be made only with results of less precise computations.

On the chart (Fig. 1) it is apparent that, within the scale of the drawing, the computations with function Ψ coincide with those obtained by the Hartree method, which reliably confirms the accuracy of either computation. In the scale of the drawing, the computations with the functions Ψ_2, Ψ_4 and by the Fok method for phase η^- also coincide. For phase η^+ agreement between the various computations is considerably poorer (curves IV through VIII), even omitting the Morse and Allis computation by Fok's method (curve VIII) whose inaccuracy for η at small energies is not established. The disagreement between results of /92 computations with the same function by Hulthen and Kohn (curves IV, V and VI, VII) also indicates the unreliability of the results and the fact that the choice of functions Ψ_2, Ψ_4 for this case was unfortunate.

The circumstance of obtaining, at the same approximation, much better results for η^- than for η^+ is understandable. Indeed, the function Ψ^- becomes zero at $r_{12} = 0$ and its behavior at small r_{12} is, consequently, of little significance in a variational computation. However, particularly in that region, the behavior of the wave function becomes especially complex. At large r_{12} the effect of polarization should be weak; the wave function at the good approximation breaks up into products of single electron functions; consequently, for function Ψ^-, Fok's method should give good results.

The computational results with function Ψ_3 present less interest; as for Schroedinger's equation, there does not exist a solution which would have the asymptotic form

$$\Psi_{\sim} \begin{cases} \psi_0(r_1)\,\dfrac{\sin(kr_2 + \eta)}{kr_2}, & r_2 \to \infty, \\ 0, & r_1 \to \infty. \end{cases} \qquad (5)$$

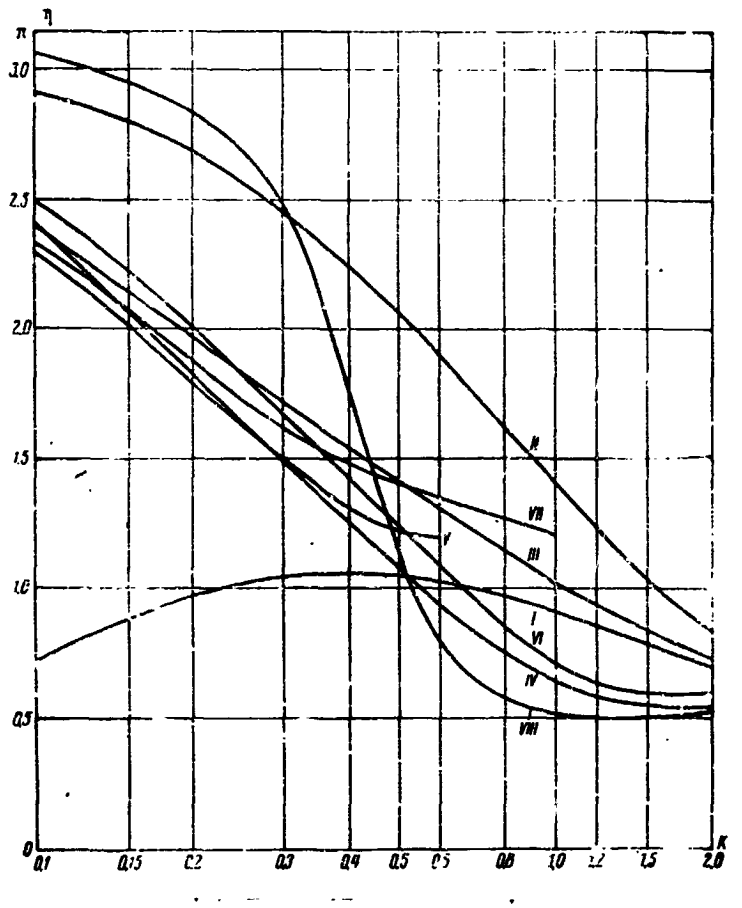

Fig. 1. Various Phase Computations for the Elastic s-Scattering of Electrons by Hydrogen Atoms

The wave number k is plotted in logarithmic scale to enable more detailed presentation of phase's behavior at small k's.

I - Computation of phase η by Hartree method; variational computation with function Ψ_1 by the methods of Hulthen and Kohn; II - Computation of phase η by Fok's method; variational computation with functions Ψ_2, Ψ_4 by the methods of Hulthen and Kohn; III - Variational computation of phase η with function Ψ_3 by methods of Hulthen and Kohn; IV - Variational computation of phase η^+ with function Ψ_2 by Hulthen's method; V - Variational computation of phase η^+ by Kohn's method; VI - Variational computation of phase η^+ with function Ψ_4 by Hulthen's method; VII - Variational computation of phase η^+ with function Ψ_4 by Kohn's method; VIII - Computation of phase η^+ by Fok's method.

At $k \to 0$ curve I tends to zero, while curves II through VIII tend to the value $\eta = \pi$.

If we were to perform a variational computation in higher approximations, adding to Ψ_3 arbitrary linear combinations of functions $\varphi_1, \cdots, \varphi_n$, which diminish at large r_1 as well as at large r_2, we should expect that the thus obtained approximate wave functions would lead at $n \to \infty$ to some linear combination of Ψ^+ and Ψ^-. Such a linear combination could not have the asymptotic form (5), as long as $\eta^+ \neq \eta^-$. It is possible, however, to require that condition (5) be satisfied at large r_2, while the coefficient at the respective term for large r_1 be minimal. It could be easily seen that this requirement is fulfilled for the linear combination $\frac{1}{\sqrt{2}} \left(\cos \frac{\eta^+ - \eta^-}{2}\right)^{-1} (\Psi^+ - \Psi^-)$ and that the phase η will be approaching/93 the limit

$$\frac{1}{2} (\eta^+ - \eta^-).$$

From Fig. 1 it can be seen that for Ψ_3 this condition is fulfilled, approximately only, at $k > 0.8$.

It is also interesting to investigate the results obtained with various approximations at $k = 0$. Taking account of polarization (Ψ_3, Ψ_4) or of exchange (Ψ_2, Ψ_4) has the result that the value of phase η^+ at $k = 0$ becomes equal to π (Fig. 1), while the computation by Hartree method and the variational computation with function Ψ_1 gives $\eta^+ (0) = 0$.

This result can be compared with the theorem proved by Levinson (Ref. 56) for the scattering of a nucleus by a central field. By that theorem the difference

$$\frac{1}{\pi} [\eta(0) - \eta(\infty)]$$

is equal to the number of fixed s-states of the nucleus in that field (if we omit the particular case when the discrete negative energy level becomes zero at the limit and coincides with the boundary of the continuous spectrum).

Levinson's theorem is fully applicable to the computation of elastic scattering of an electron by hydrogen by Hartree's method. That method, as is known, does not give the fixed condition for the negative ion of hydrogen H^- and, correspondingly, η (0) in Hartree's method becomes zero.

Allowing for polarization [for instance, the variational computation with the function $e^{-\alpha(r_1+r_2)}(1 + \beta r_{12})$] leads to the appearance of the fixed state for H^-. From Fig. 1 it is seen that the variational computation for s-scattering with consideration of polarization (Ψ_3) accordingly leads to $\eta(0) = \pi$. It is easily demonstrated that taking exchange into account also enables us to obtain the fixed state of H^-. For instance, the variational computation with function

$$\psi = e^{-\alpha r_1 - \beta r_2} + e^{-\alpha r_2 - \beta r_1}, \tag{6}$$

gives the energy of the fixed state - 0.013. It is obvious that this value will only improve if we solved Fok's equation derived from the minimum requirement for the functional /94

$$E = -\frac{1}{2}\int\int \psi L \psi \, d\tau_1 \, d\tau_2,$$

$$\psi = \phi_1(r_1)\,\phi_2(r_2) + \phi_1(r_2)\,\phi_2(r_1), \tag{7}$$

on condition of normalization of ψ. The results of Morse and Allis computations are equivalent to the variational computation of s-scattering with function

$$\Psi = \frac{1}{\sqrt{2\pi}}\left(F(r_1)e^{-r_2} + F(r_2)e^{-r_1}\right), \tag{8}$$

analogous to function (7). Correspondingly, in this approximation $\eta^+(0) = \pi$. The same result is obtained at a variational computation with function Ψ_2 in which symmetry is included in the simplest way and which is analogous to function (6) for the discrete spectrum.

Thus, the comparison of variational computations for the discrete and continuous spectra of a system of two electrons in the field of a proton shows that, if consideration of a certain effect leads to the appearance of fixed state for the discrete spectrum, then consideration of the same effect in a scattering problem will lead to the increase of the value $\eta(0)$ by π.

This statement is not rigorous, as the theorem of Levinson is derived only for scattering by a force-center. Its extension to the

multi-body problem would be a matter of great interest. We will note that such an extension does not appear trivial, as for η^- the theorem in its former form is not fulfilled. Indeed, all approximations yield for $\eta^-(0)$ the value π; at the same time it may be stated with certainty, that the fixed state of H^- with antisymmetrical wave function does not exist. This can be explained qualitatively by the fact that in Levinson's theorem account must be taken, not only of permitted states, but also those forbidden by the Pauli principle. The same assumption has already found expression in Swan's paper (Ref. 57).

A comparison of the Hulthen and Kohn method has proved that /95 the Hulthen method yields a somewhat better result for a phase; however, as shown in Section 12, a noticeable diversion between both methods points toward the disagreement of the original system of equations; therefore, the results cease to be reliable. A check of the Hulthen method calculations has been conducted with the help of an integral identity for the functions Ψ_1, Ψ_2. It is pointed out in Section 12 that in the selected function φ_1 the integral identity is equivalent to the first equation of the system (12.16), and that solving of this equation indicates only the coincidence of the results of the Hulthen and Kohn methods.

We will also mention that the assertion by Massey and Moiseiwitsch (Ref. 21, p. 488) is not true that there is no integral identity for the general wave function with consideration of polarization. From the results of Section 12 it can be seen that the integral identity is obtained automatically from the variational principle by means of substituting in the functional the functions of null approximation instead of the function Ψ_1 (the Born-Oppenheimer method); and instead of the function Ψ_2, substitute the accurate function. In that case,we will obtain for the s-scattering

$$\operatorname{tg}\eta^{\pm} = \frac{k}{4\pi}\iint \Psi^{\pm} L\psi_0(r_1)\frac{\sin kr_2}{kr_2}\,d\tau_1\,d\tau_2 =$$

$$= \frac{1}{4\pi}\iint \Psi^{\pm}(r_1, r_2, r_{12})\left(\frac{2}{r_2} - \frac{2}{r_{12}}\right)\psi_0(r_1)\sin kr_2\,\frac{d\tau_1 d\tau_2}{r_2}. \quad (9)$$

Here $\Psi_0 = \frac{1}{\sqrt{\pi}} e^{-r}$, and the function $\Psi^{\pm}$ is an accurate solution to the equation $L\Psi^{\pm} = 0$ and has the same asymptotic form as the function in equations (2) and (4). If the energy of the electrons is sufficient to excite an atom, then spherical waves, which correspond to the inelastic scattering, will also appear in the asymptotic form of the function $\Psi^{\pm}$, and therefore, the function $\Psi^{\pm}$ is not essential. In that case it is /96 easy to obtain an identity [which is analogous to (9)] directly for the scattering amplitude of the spherical wave.

Variational calculations for collisions of electrons with hydrogen atoms were also conducted with the Schwinger method (Refs. 42, 45, 46); however, the results differ from those of Massey and Moiseiwitsch results, and obviously are less reliable.

CHAPTER III

THE SYMMETRY OF FUNCTIONALS, THE PRINCIPLE OF SEPARATE EQUILIBRIUM, THE UNITARITY OF THE SCATTERING OPERATOR

§16. Symmetry of Functionals in the Hulthen and Kohn Methods

The operators being considered in quantum mechanics are, as a rule, self conjugated. This means that in the case of a self conjugated operator, the following equation should be evaluated

$$\int \psi_1^* L\psi_2 \, d\tau = \int \psi_2 \, (L\psi_1)^* \, d\tau, \tag{1}$$

for any given two functions ψ_1 and ψ_2 which satisfy the specified conditions. It is obvious that this determination makes sense if there are given the apparent form of the operator as well as the multitude of functions in relation to which this operator is self conjugated. The operator H - E, which is being considered in the variational principles by Hulthen and Kohn, is self conjugated for functions which are twice differentiated and integrated to a square. However, for these functions which we have substituted in the functional I (see, for instance, 6.17) and which cannot be integrated to a square, the equality

$$I(\Phi_2, \Phi_1) = 1(\Phi_1, \Phi_2), \tag{2}$$

can, generally speaking, not be evaluated. For instance, we have seen/98 during the deriviation of the variational principle by Kohn that the variance

$$I(\Psi_1, \delta\Psi_2) - I(\delta\Psi_2, \Psi_1) = \int (\Psi_1 \nabla^2 \delta\Psi_2 - \delta\Psi_2 \nabla^2 \Psi_1) \, d\tau \tag{3}$$

does not convert into 0 since, after utilizing the Green formula, the surface integral has the final value within its boundaries.

As a result of an asymmetry the variation of the functional in the Kohn principle depends only on the variation of the function Ψ_1, that is on $\delta\Psi_1$, and it does not depend on $\delta\Psi_2$. This result can also be obtained in the Hulthen principle, if we apply, in the capacity of an original functional, a bilineal functional

$$I(\varphi_2, \varphi_1) = \int_0^\infty \varphi_2 \left(\frac{d^2}{dr^2} + k^2 - V\right) \varphi_2 \, dr, \tag{4}$$

where

$$\varphi_i(0) = 0, \quad \varphi_i \sim A_i \sin(kr + \eta_i) \quad (i = 1,2). \tag{5}$$

In the case when the functions $\varphi_1 = \psi_1$ and $\varphi_2 = \psi_2$ satisfy the Schroedinger equation, the functional converts into 0 and, obviously, it does not depend on the variation of the function φ_2. The variation of φ_1 yields the previous formula after integration by parts

$$\delta I(\psi_2, \psi_1) = - A_1 A_2 k \delta\eta_1, \tag{6}$$

where $\delta\eta_1$ are the phase variations of the function ψ_1.

Thus, the functions Ψ_1 and Ψ_2 are included unequally in the variational principles by Hulthen and Kohn.

If we should substitute, in place of the functions φ_1 and φ_2, a linear combination of certain n of a given function $v_i(r)$

$$\varphi_1 = \sum c_i v_i(r); \quad \varphi_2 = \sum c_i' v_i(r);$$

$$v_i(0) = 0, \quad i = 1, 2, \cdots, n;$$

$$v_j(r) \to 0 \text{ when } r \to \infty. \quad j = 3, 4, \cdots, n;$$

$$v_1(r) \sim \sin kr, \quad v_2(r) \sim \cos kr, \tag{7}$$

then the functional $I(\varphi_2, \varphi_1)$ will be put down in a bilinear form /99

$$I = \sum_{i,j=1}^{n} I_{ij} c_i' c_j, \quad I_{ij} = \int_0^\infty v_i \left(\frac{d^2}{dr^2} + k^2 - V\right) v_j \, dr. \tag{8}$$

As a result of the operators non-self conjugation the condition

$$I_{ij} = I_{ji}, \tag{9}$$

is generally speaking not fulfilled. In the given case only

$$I_{21} - I_{12} = k, \tag{10}$$

and the remaining coefficients I_{ij} are symmetric.

The formula (6) may be put down in form analogous to (12.15),

$$\delta I = k\,(c_2'\delta c_1 - c_1'\delta c_2). \tag{11}$$

It is easily conceivable that the system of equations derived in this case for the coefficients c_i, c_i', are identical and coincide with the system of equations (12.16). Thus, in the final calculation the symmetry in this case is preserved. This result can be easily obtained also during a more general method of selection of functions.

It is obvious generally that the requirement of self conjugation on the part of the operator H - E or the requirement (2) on the part of the symmetry of the functional $I(\varphi_2, \varphi_1)$ should place determined limitations on the functions φ_1 and φ_2, which are substituted in the functional. As we will observe later, these limitations are closely related to the principle of separate equilibrium in quantum mechanics and also to the unitarity of the scattering operator.

§17. Passage of a Particle Through a Potential Barrier and the Symmetry of the Variational Functional

We will consider a simple one dimensional problem on the passage of a particle through a potential barrier. The Schroedinger equation has the following form in this case:

$$\left(\frac{d^2}{dx^2} + k^2 - V(x)\right)\psi(x) = 0. \tag{1}$$

We will assume that V (x) is limited and that it decreases /100 rapidly (faster than $1/x^2$) when $|x| \to \infty$. The region located to the left of the potential barrier will be defined by index 1, and the region to the right will be defined by index 2.

We will consider the flux of particles which fall to the left (from region 1) on the potential barrier. The wave function in this case will have the following asymptotic form

$$\psi_1 \Big|_{x \to -\infty} \sim e^{ikx} + a_{11} e^{-ikx}; \quad \psi_1 \Big|_{x \to +\infty} \sim a_{12} e^{ikx}. \tag{2}$$

It is obvious that the function ψ_1^* will also be the solution to the equation. It is also possible to consider the flux of particles which fall on the potential barrier to the right (from region 2). We will define the wave function of this problem as ψ_2.

The asymptotic form of the wave functions ψ_1, ψ_2, ψ_1^*, ψ_2^* is illustrated in Table 4.

TABLE 4

	Region 1, $x \to -\infty$	Region 2, $x \to \infty$
ψ_1	$e^{ikx} + a_{11} e^{-ikx}$	$a_{12} e^{ikx}$
ψ_2^*	$e^{-ikx} + a_{11}^* e^{ikx}$	$a_{12}^* e^{-ikx}$
ψ	$a_{21} e^{-ikx}$	$e^{-ikx} + a_{22} e^{ikx}$
ψ_2^*	$a_{21}^* e^{ikx}$	$e^{ikx} + a_{22}^* e^{-ikx}$

The square of the modulus of coefficients of transition a_{ij} determines the transition probability of particles from the region i to the region j.

The variational principle for this problem might be obtained from the consideration of the functional

$$I(\varphi_2, \varphi_1) = \int_{-\infty}^{+\infty} \varphi_2 \left(\frac{d^2}{dx^2} + k^2 - V \right) \varphi_1 \, dx, \tag{3}$$

where φ_1, φ_2 have the following asymptotic form /101

$$\varphi_i \sim a_i e^{ikx} + b_i e^{-ikx} \tag{4}$$

with certain arbitrary coefficients a, b, which differ for various functions and regions.

By placing specified limitations on the asymptotic behavior of the functions φ_1 and φ_2, we can obtain a stationary expression for the transition coefficients a_{ik}.

We will explain which effect can be obtained from the requirement of symmetry of the functional in regard to the displacement of the functional φ_1, φ_2

$$I(\varphi_1, \varphi_2) = I(\varphi_2, \varphi_1), \tag{5}$$

it is obvious that this requirement is fulfilled for the sake of accurate solutions to the Schroedinger equation, since in that case both parts of the equation convert into 0. We have

$$I(\varphi_1, \varphi_2) - I(\varphi_2, \varphi_1) =$$

$$= \int_{-\infty}^{+\infty} (\varphi_1\varphi_2'' - \varphi_1''\varphi_2)\, dx = (\varphi_1\varphi_2' - \varphi_1'\varphi_2)\Big|_{-\infty}^{+\infty} = 0. \tag{6}$$

If we should substitute now in place of the function φ_1, φ_2 the functions ψ_1, ψ_1^*, ψ_2, ψ_2^*, then we obtain a number of correlations between the coefficients a_{ij}.

Of course, these correlations might be obtained also in a simpler way, since from the four solutions to ψ_1, ψ_1^*, ψ_2, and ψ_2^* only two represent linear independencies. Therefore, the functions ψ_2 and ψ_2^* might be obtained as linear combinations of the function ψ_1 and ψ_1^* and, respectively, the coefficients a_{21} and a_{22} might be expressed by a_{11} and a_{12}.

However, the method applied here leads to the same result and allows us to derive a generalization for more complicated problems in the theory of collisions.

Equation (6) also follows directly from the fact that the Vronsky denominator does not depend on x for two solutions to equation (1).

By combining four equations in pairs we obtain six possible conditions of symmetry: /102

$$\begin{aligned}
&1)\ I(\psi_1, \psi_1^*) = I(\psi_1^*, \psi_1), && 2)\ I(\psi_2, \psi_2^*) = I(\psi_2^*, \psi_2),\\
&3)\ I(\psi_1, \psi_2) = (\psi_2, \psi_1), && 4)\ I(\psi_1^*, \psi_2^*) = I(\psi_2^*, \psi_1^*),\\
&5)\ I(\psi_1, \psi_2^*) = I(\psi_2^*, \psi_1), && 6)\ I(\psi_1^*, \psi_2) = I(\psi_2, \psi_1^*).
\end{aligned} \tag{7}$$

It is obvious that the third and fourth as well as the fifth and sixth conditions of symmetry are equivalent.

By substituting in formula (6) the asymptotic form of the function, we obtain from the first and second conditions the equation

$$\begin{aligned}
|a_{11}|^2 + |a_{12}|^2 &= 1,\\
|a_{21}|^2 + |a_{22}|^2 &= 1.
\end{aligned} \tag{8}$$

from the third and fourth conditions, we have

$$a_{12} = a_{21}. \tag{9}$$

Finally, from the fifth and sixth conditions we obtain

$$a_{11}a_{21}^* + a_{12}a_{22}^* = 0. \tag{10}$$

The equations (8) express the law of current stability for states which are characterized by the wave functions ψ_1 and ψ_2. From equation (9) it follows that the probabilities are identical that the particles will pass through a potential barrier from left to right and from right to left; that is, there follows the reversibility principle or the principle of separate equilibrium for the given problem. It follows, from this equation, that the phases of complex transition coefficients a_{12} and a_{21} are equal in regard to each other. Equation (10) does not make such physical sense. This equation combines the phases of the coefficients a_{11}, a_{12}, and a_{22}.

Equations (8), (9), and (10) express the condition of symmetry and the unitarity of the matrix /103

$$S = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}. \qquad (11)$$

We will consider somewhat more in detail the sense of this matrix.

Let us assume that, at the starting moment, we had in region 1 a wave pocket, which was removed at some distance from the potential barrier, and which is traveling toward this barrier. Then, after a scattering, we obtain two wave pockets with determined phases and amplitudes which travel to the right and to the left from the potential barrier. Such a condition is obtained during the motion of the wave pocket to the right of region 2. We assume, thereby, that the wave pocket is so wide that it can be considered as being "monochromatic", and we may therefore disregard any events which are related to spreading.

It is possible to construct a scattering operator (Ref. 27), which transforms the wave function before scattering into a wave function after scattering. The wave function of a particle before and after scattering might be characterized in the given case by complex wave amplitudes, which travel to the right and to the left: $\psi \sim c_1 e^{ikx} + c_2 e^{-ikx}$.

In such a sense the above considered matrix will actually be the scattering operator. The scattering operator determines fully "the scattering" properties of the potential barrier.

Thus, we can see that the problem on the symmetry of the functional $I(\varphi_2, \varphi_1)$, in relation to the displacement of the functions φ_1, φ_2 in the given case, is closely related to the principle of reversibility or the separate equilibrium and also to the unitarity of the scattering operator. We will explain further that all these considerations might be broadened to include more general problems in the collision theory.

§18. On One Identity for the Scattering Amplitude of Particles by a Central Field /104

The solution to the problem on scattering of a flux of particles by a central field V(r) leads to the following expression for the scattering amplitude:

$$f(\vec{v}\cdot\vec{n}) = \frac{1}{2i}\sum_{\ell=0}^{\infty}(2\ell+1)\left(e^{2i\eta_\ell}-1\right)P_\ell(\vec{v}\cdot\vec{n}) =$$

$$= \frac{1}{2i}\sum_{\ell=0}^{\infty}(2\ell+1)\,b_\ell P_\ell(\vec{v}\cdot\vec{n}). \qquad (1)$$

It is obvious from this formula that the scattering amplitude should not be selected in an arbitrary manner, i.e., not for all functions $f(\vec{v}\cdot\vec{n})$ is it possible to find such a potential $V(r)$, for which f would have been the scattering amplitude.

The amplitudes of the convergent and divergent waves should equal each other for every term in the resolutions (4.3) of the wave function Ψ. It follows from this requirement that the phases η_ℓ should be material, and thus the coefficients of the resolution b_ℓ of the function f are not arbitrary. These coefficients should satisfy the correlation

$$b_\ell + 1 = e^{2i\eta_\ell},\ (b_\ell+1)(b_\ell^*+1) = 1,\ b_\ell b_\ell^* + b_\ell + b_\ell^* = 0. \qquad (2)$$

We will multiply the last of these equations by $(2\ell+1)P_\ell(\vec{v}\cdot\vec{v}')$ and we will summarize this by all ℓ. Then

$$\sum_{\ell=0}^{\infty} b_\ell b_\ell^*(2\ell+1)P_\ell(\vec{v}\cdot\vec{v}') +$$

$$+\sum_{\ell=0}^{\infty}(b_\ell+b_\ell^*)(2\ell+1)P_\ell(\vec{v}\cdot\vec{v}') = 0, \qquad (3)$$

$$\sum_{\ell=0}^{\infty} b_\ell b_\ell^*(2\ell+1)P_\ell(\vec{v}\cdot\vec{v}') +$$

$$+ 2i\left[f(\vec{v}\cdot\vec{v}') - f^*(\vec{v}\cdot\vec{v}')\right] = 0. \qquad (4)$$

Later we will form the integral

$$\int f^*(\vec{v}'\cdot\vec{n})\,f(\vec{v}\cdot\vec{n})\,d\omega, \qquad (5)$$

where the integration is conducted in all directions of the unit vector $\vec{n}$. By utilizing (1), we obtain /105

$$\int f^* (\vec{v}' \cdot \vec{n}) f (\vec{v} \cdot \vec{n}) d\omega =$$

$$= \frac{1}{4} \sum_{\ell=0}^{\infty} (2\ell + 1)^2 b_\ell^* b_\ell \int P_\ell (\vec{v} \cdot \vec{n}) P_\ell (\vec{v}' \cdot \vec{n}) d\omega. \quad (6)$$

The integral can be easily calculated if we utilize the theorem of addition (9.4). We obtain

$$\int f^* (\vec{v}' \cdot \vec{n}) f (\vec{v} \cdot \vec{n}) d\omega = \frac{\pi}{4} \sum_{\ell=0}^{\infty} (2\ell + 1) b_\ell^* b_\ell P_\ell (\vec{v} \cdot \vec{v}'). \quad (7)$$

By substituting this equation in the formula (4), we finally have

$$\frac{1}{4\pi} \int f^* (\vec{v}' \cdot \vec{n}) f (\vec{v} \cdot \vec{n}) d\omega = \frac{1}{2i} [f (\vec{v} \cdot \vec{v}') - f^* (\vec{v}' \cdot \vec{v})] =$$

$$= \operatorname{Im} [f(\vec{v} \cdot \vec{v}')]. \quad (8)$$

This identity should be carried out at any given orientation of the unit vectors $\vec{v}$, $\vec{v}'$. In a specific case when $v = v'$, we obtain

$$\operatorname{Im} f (\vec{v} \cdot \vec{v}) = \frac{1}{4\pi} \int |f (\vec{v} \cdot \vec{n})|^2 d\omega = \frac{\sigma}{4\pi k^2}, \quad (9)$$

where σ is the full effective cross-section.

Thus, the imaginary part of the amplitude of scattering at a 0 angle is proportional to the full effective cross-section. For a differentially effective cross-section, we might herefrom obtain the inequality

$$\lim_{\theta \to 0} \sigma (\vartheta) \geq \frac{k^2 \sigma^2}{16\pi^2}, \quad (10)$$

where θ is the angle between the vectors $\vec{v}$, $\vec{v}'$; that is, the inclination angle.

As we will see further, formulae (8), (9), and (10) might be generalized also to more complicated problems in the theory of collisions. /106

Equation (8) for the given problem is analogous to the equations (8) and (10) of the preceding section and is also related to the unitarity of the scattering operator.

We will now clarify whether formula (8) for scattering amplitude f (calculated by Born's method) will be carried out. In that case $f(\vec{v} \cdot \vec{n})$ is clearly expressed through the potential V(r) (10.28)

$$f(\vec{v} \cdot \vec{n}) = -k \int_0^\infty V(r) \frac{\sin qr}{qr} r^2 dr;$$

$$q = 2k \sin \frac{\theta}{2}; \quad \vec{v} \cdot \vec{n} = \cos \theta. \tag{11}$$

We can see that the scattering amplitude in this approximation is substantial, and thus the right part of the formula (8) converts into 0. In the meantime, the left part of the formula (8) is known to be different from 0, for instance when f = 0.

However, it is essential in Born's method that the scattering amplitude be low: $f(\theta) < 1$. From this, it follows that the left part of formula (8) is of the second order of smallness; then, during its calculation with the Born method, the terms of the second order of smallness in its right part are dropped as in the case of amplitude f. Thus, at large values of k, the imaginary part of the scattering amplitude f is much less substantial and a check of formula (8) can be conducted only through the utilization of the formula of the second approximation in the Born method.

We will mention that the principle of separate equilibrium, which was expressed in the preceding section by formula (9), is carried out here in a trivial manner, since from the spherical symmetry of the problem it followed directly that $f(\vec{v}, \vec{v}')$ depends only on the angle between the vectors $\vec{v}$, $\vec{v}'$, and consequently

$$f(\vec{v}, \vec{v}') = f(-\vec{v}', -\vec{v}), \tag{12}$$

that is, the probability of scattering of particles from the direction/107 v toward the direction v' and from the direction $-v'$ in the direction of $-v$ is reciprocally equal.

§19. General Problem on Scattering by a Potential Field and the Symmetry of a Functional

In the case of scattering of particles by a field which does not have a spherical symmetry, the scattering amplitude $f(\vec{v}, \vec{n})$ depends on the orientation of both unit vectors $\vec{v}$, $\vec{n}$ and not only on the angle between them.

We will consider the functional

$$I(\varphi_2, \varphi_1) = \int \varphi_2 (\nabla^2 + k^2 - V) \varphi_1 \, d\tau, \tag{1}$$

which is the original functional for the deriviation of the Kohn variational principle. This functional has a determined value for the functions φ_1, φ_2, which have in turn a common asymptotic form

$$\varphi_i \sim e^{ik\vec{v}_i \cdot \vec{r}} + F_i(n) \frac{e^{ikr}}{kr}. \tag{2}$$

The Ψ_1 and Ψ_2 functional converts into 0 for accurate solutions to the Schroedinger equation.

As was already metnioned, the functional (1) is, generally speaking, non-symmetric in regard to the displacement of the functions φ_1, φ_2. Analogously to the way that this was done in Section 2, we acquire the symmetry of the function

$$I(\varphi_1, \varphi_2) = I(\varphi_2, \varphi_1), \tag{3}$$

and we will clarify which conditions should be placed on the function so that these requirements would be fulfilled.

Equation (3) may be put down in the following form

$$\int (\varphi_1 \nabla^2 \varphi_2 - \varphi_2 \nabla^2 \varphi_1) \, d\tau = 0, \tag{4}$$

or, by utilizing the Green formula /108

$$\lim_{R \to \infty} \int_{r=R} \left(\varphi_1 \frac{\partial}{\partial r} \varphi_2 - \varphi_2 \frac{\partial}{\partial r} \varphi_1 \right) dS = 0. \tag{5}$$

In this case the integration is conducted by the sphere of the radius R. We may thereby utilize the asymptotic form (2) of the functions φ_1 and φ_2.

We will lay out these asymptotic expressions into a row by spherical functions

$$\varphi_i \sim \sum_{\ell=0}^{\infty} \left[(2\ell + 1) \sqrt{\frac{\pi}{2kr}}\, I_{\ell+1/2}\,(kr)\, P_\ell\,(\vec{v}_i \cdot \vec{n}) + \right.$$

$$\left. + Y_\ell^{(i)}\,(\vec{n})\, \frac{e^{ikr}}{kr} \right] . \qquad (6)$$

Here, $Y_\ell^{(i)}$ are certain spherical functions of the order ℓ, which are obtained during the solution into a row of functions F_1, F_2,*

$$F_i = \sum_{\ell=0}^{\infty} Y_\ell^{(i)}\,(\vec{n}) . \qquad (7)$$

If we should substitute solution (6) in formula (5), then in result of the orthogonality of the spherical functions we will have a simple sum instead of a dual sum under the integral.

We will consider the ℓ term of this sum; thereby, instead of the Bessel function $I_{\ell+1/2}$, we will substitute its asymptotic form. We have

$$\left\{ \frac{2\ell + 1}{2ikr} \left[e^{ikr} - (-)^\ell e^{-ikr} \right] P_\ell\,(\vec{v}_1 \cdot \vec{n}) + Y_\ell^{(1)}\,(\vec{n})\, \frac{e^{ikr}}{kr} \right\} \times$$

$$\times \left\{ \frac{2\ell + 1}{2r} \left[e^{ikr} + (-)^\ell e^{-ikr} \right] P_\ell\,(\vec{v}_2 \cdot \vec{n}) + ikY_\ell^{(2)}\,(\vec{n})\, \frac{e^{ikr}}{kr} \right\} -$$

$$- \left\{ \frac{2\ell + 1}{2ikr} \left[e^{ikr} - (-)^\ell e^{-ikr} \right] P_\ell\,(\vec{v}_2 \cdot \vec{n}) + Y_\ell^{(2)}\,(\vec{n})\, \frac{e^{ikr}}{kr} \right\} \times$$

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*It is obvious that Y_ℓ^i are not standardized and are generally speaking linear combinations of auto-normalized spherical functions $Y_{\ell m}$.

/109

$$\times \left\{\frac{2\ell + 1}{2r} \left[e^{ikr} - (-)^{\ell} e^{-ikr}\right] P_{\ell} (\vec{v}_1 \cdot \vec{n}) + ikY_{\ell}^{(1)} (\vec{n}) \frac{e^{ikr}}{kr}\right\} =$$

$$= - \frac{2\ell + 1}{r^2} (-)^{\ell} [P_{\ell} (\vec{v}_1 \quad \vec{n}) Y_{\ell}^{(2)} (\vec{n}) -$$

$$- P_{\ell} (\vec{v}_2 \cdot \vec{n}) Y_{\ell}^{(1)} (\vec{n})]. \qquad (8)$$

It is possible in integration to utilize once again the addition theorem

$$\int Y_{\ell} (\vec{n}) P_{\ell} (\vec{v} \cdot \vec{n}) d\omega = \frac{4\pi}{2\ell + 1} Y_{\ell} (\vec{v}). \qquad (9)$$

In such a form the theorem is applicable for any given spherical function on the order of ℓ. After integration, we obtain

$$\sum_{\ell=0}^{\infty} (-)^{\ell} Y_{\ell}^{(1)} (\vec{v}_2) = \sum_{\ell=0}^{\infty} (-)^{\ell} Y_{\ell}^{(2)} (\vec{v}_1), \qquad (10)$$

$$\sum_{\ell=0}^{\infty} Y_{\ell}^{(1)} (-\vec{v}_2) = \sum_{\ell=0}^{\infty} Y_{\ell}^{(2)} (-\vec{v}_1), \qquad (11)$$

since the constancy of the function $Y_{\ell} = (-)^{\ell}$.

Thus,

$$F_1 (-\vec{v}_2) = F_2 (-\vec{v}_1). \qquad (12)$$

Now if we substitute, in place of the functions φ_1, φ_2, the accurate solutions to the Schroedinger equation Ψ_1, Ψ_2 with the scattering amplitudes $f(\vec{v}_1, \vec{n})$, $f(\vec{v}_2, \vec{n})$, we will obtain a formulation of the separate equilibrium principle for the given problem

$$f (\vec{v}_1, -\vec{v}_2) = f (\vec{v}_2, -\vec{v}_1). \qquad (13)$$

We will consider the requirement

$$I(\varphi_1^*, \varphi_2) = I(\varphi_2, \varphi_1^*), \tag{14}$$

which obviously should also be fulfilled in the case of the accurate wave functions Ψ_1, Ψ_2. By acting precisely in the same manner, we /110 come to an analogous expression for the ℓ term in the surface integral

$$\left\{\frac{2\ell+1}{-2ikr}\left[e^{-ikr} - (-)^{\ell}e^{ikr}\right] P_{\ell}(\vec{v}_1 \cdot \vec{n}) + Y_{\ell}^{(1)*}(\vec{n})\frac{e^{-ikr}}{kr}\right\} \times$$

$$\times \left\{\frac{2\ell+1}{2r}\left[e^{ikr} + (-)^{\ell}e^{ikr}\right] P_{\ell}(\vec{v}_2 \cdot \vec{n}) + ikY_{\ell}^{(2)}(\vec{n})\frac{e^{ikr}}{kr}\right\} -$$

$$- \left\{\frac{2\ell+1}{2ikr}\left[e^{ikr} - (-)^{\ell}e^{-ikr}\right] P_{\ell}(\vec{v}_2 \cdot \vec{n}) + Y_{\ell}^{(2)}(\vec{n})\frac{e^{ikr}}{kr}\right\} \times$$

$$\times \left\{\frac{2\ell+1}{-2r}\left[-e^{-ikr} - (-)^{\ell}e^{ikr}\right] P_{\ell}(\vec{v}_1 \cdot \vec{n}) - Y_{\ell}^{(1)*}(\vec{n})\frac{e^{-ikr}}{kr}\right\} =$$

$$= -\frac{2\ell+1}{kr^2} P_{\ell}(\vec{v}_1 \cdot \vec{n}) Y_{\ell}^{(2)}(\vec{n}) + \frac{2\ell+1}{kr^2} P_{\ell}(\vec{v}_2 \cdot \vec{n}) Y_{\ell}^{(1)*}(\vec{n}) +$$

$$+ \frac{2i}{kr^2} Y_{\ell}^{(1)*}(\vec{n}) Y_{\ell}^{(2)}(\vec{n}). \tag{15}$$

By utilizing again the addition theorem and considering that

$$\int F_1^*(\vec{n}) F_2(\vec{n})\, d\omega = \sum_{\ell=0}^{\infty} \int Y_{\ell}^{(1)*}(\vec{n}) Y_{\ell}^{(2)}(\vec{n})\, d\omega, \tag{16}$$

we obtain the formula

$$\frac{4\pi}{k}\left[F_1^*(\vec{v}_2) - F_2(\vec{v}_1)\right] + \frac{2i}{k}\int F_1^*(\vec{n}) F_2(\vec{n})\, d\omega = 0. \tag{17}$$

For an accurate scattering amplitude, we obtain herefrom

$$\frac{1}{2i}\left[f\left(\vec{v}_2, \vec{v}_1\right) - f^*\left(\vec{v}_1, \vec{v}_2\right)\right] = \frac{1}{4\pi}\int f^*\left(\vec{v}_1, \vec{n}\right) f\left(\vec{v}_2, \vec{n}\right) d\omega. \quad (18)$$

Thus, we have acquired an identical identity for scattering amplitude as we did in Section 3. In this case the identity was derived at more general assumptions, since the potential is, generally speaking, not considered to be spherically symmetrical.

§20. The Symmetry of the Interaction Operator and of the Scattering Amplitude. The Scattering Matrix. The Variational Principle Related to the Correlation of Unitarity

/111

It was actually assumed during the deriviation of the basic formulas in the preceding section that the operator of interaction V is substantial and self conjugated.

If these conditions are not fulfilled, then the problem on the scattering of particles, in which the interaction with the scatterer is characterized by operators V, V', V^*, V^+, will yield different scattering amplitudes which we will define, respectively, f, $f^{(')}$, $f^{(*)}$, $f^{(+)}$. The conditions of symmetry derived in the preceding section lead, in this given case, toward the establishment of correlations between these amplitudes. In place of correlation (13), we obtain with the same method

$$f\left(\vec{v}_1, \vec{v}_2\right) = f^{(')}\left(-\vec{v}_2, -\vec{v}_1\right). \quad (1)$$

Thus, the principle of separate equilibrium is fulfilled, if operator V is symmetrical, that is if $V = V'$. The requirement of self conjugation is not compulsory. Let us assume, for instance, that operator V is a complex function of coordinates; then the number of particles will not be preserved during scattering. However, in spite of all this the principle of separate equilibrium will be fulfilled, since operator V is diagonal in the x-presentation and, consequently, also symmetrical. If operator V is self conjugated, then $V' = V^*$, $f^{(')} = f^{(*)}$, and consequently

$$f\left(\vec{v}_1, \vec{v}_2\right) = f^{(*)}\left(-\vec{v}_2, -\vec{v}_1\right), \quad (2)$$

that is, the principle of separate equilibrium combines the scattering amplitudes of the particles by two complex conjugated fields.*

In place of correlation (19.18) we obtain, in an analogous way, the following /112

$$\frac{1}{2i}\left[f^{(+)}(\vec{v}_2, \vec{v}_1) - f^{*}(\vec{v}_1, \vec{v}_2)\right] =$$

$$= \frac{1}{4\pi}\int f^{*}(\vec{v}_1, \vec{n})\, f^{(+)}(\vec{v}_2, \vec{n})\, d\omega. \qquad (3)$$

Thus, correlation (19.18) is fulfilled, if operator V is self conjugated.

These formulas might be recorded in much simpler form, if we introduce the operator or the scattering matrix

$$S(\vec{v}_1, \vec{v}_2) = \delta(\vec{v}_1 - \vec{v}_2) + \frac{2i}{4\pi} f(\vec{v}_1, \vec{v}_2). \qquad (4)$$

Then correlations (19.13) and (19.18) will be stated as follows

$$S(\vec{v}_1, \vec{v}_2) = S(-\vec{v}_2, -\vec{v}_1), \qquad (5)$$

$$\int S^{*}(\vec{v}_1, \vec{n})\, S(\vec{v}_2, \vec{n})\, d\omega = \delta(\vec{v}_1 - \vec{v}_2) \qquad (6)$$

Thus, these correlations actually express the properties of symmetry and unitarity of matrix S, which is analogous to matrix S in Section 17.

Contrary to the simpler example in Section 17, we have, in this case, a continuous association of initial and final states, which are characterized by the direction of motion of the falling and scattering particles, that is, by vectors $\vec{v}_1$ and $\vec{v}_2$.

If the scattering matrixes which correspond to the amplitudes $f^{(')}$, $f^{(*)}$ and $f^{(+)}$, were defined as $S^{(')}$, $S^{(*)}$ and $S^{(+)}$ then, instead of correlations (3) and (4), we would obtain

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*We will mention that, generally speaking, $f' \neq f^{(')}$, $f^{*} \neq f^{(*)}$, and $f^{+} \neq f^{(+)}$.

$$S(\vec{v}_1, \vec{v}_2) = S^{(')}(-\vec{v}_2, -\vec{v}_1), \tag{7}$$

$$\int S^*(\vec{v}_1, \vec{n})\, S^{(+)}(\vec{v}_2, \vec{n})\, d\omega = \delta(\vec{v}_1 - \vec{v}_2). \tag{8}$$

It is obvious that the variational principle by Hulthen-Kohn (considered in Chapters I and II) is closely related to the principle of separate equilibrium which was derived here.

It can be easily proved that the principle of separate equilibrium is automatically fulfilled, when the approximate functions ψ_1 and ψ_2, which correspond to the initial and final states, are used in a variational calculation of the scattering amplitude. Actually, if operator V is symmetrical, we obtain for $f(\vec{v}_1, -\vec{v}_2)$ and $f(\vec{v}_2, -\vec{v}_1)$, the following approximate expression: /113

$$f(\vec{v}_1, -\vec{v}_2) = \tilde{f}(\vec{v}_1, -\vec{v}_2) + \frac{k}{4\pi}\int \tilde{\Psi}_2 (\nabla^2 + k^2 - V)\, \tilde{\Psi}_1\, d\tau,$$

$$f(\vec{v}_2, -\vec{v}_1) = \tag{9}$$

$$= \tilde{f}(\vec{v}_2, -\vec{v}_1) + \frac{k}{4\pi}\int \tilde{\Psi}_1 (\nabla^2 + k^2 - V)\, \tilde{\Psi}_2\, d\tau.$$

By subtracting these equations we obtain, according to (19.12), 0 in the right part; thus, the principle of separate equilibrium is fulfilled for the approximate amplitude f independently from the fact if the principle for the corresponding amplitudes $\tilde{f}(\vec{v}_1, -\vec{v}_2)$, $\tilde{f}(\vec{v}_2, -\vec{v}_1)$, in the approximate functions $\tilde{\Psi}_1$, $\tilde{\Psi}_2$, was fulfilled.

Analogous results might be obtained also in the case of more complicated problems.

We will now formulate the variational principle which is directly related with the correlation of unitarity conditions (19.18). For this purpose we will construct the functional

$$K = \int \Psi_2^* (\nabla^2 + k^2 - V)\, \Psi_1\, d\tau. \tag{10}$$

We assume, thereby, that operator V is self conjugated. Calculating normally the variation of this functional, in regard to the accurate

wave functions Ψ_1 and Ψ_2, we obtain

$$\delta K = -\frac{4\pi}{k}\,\delta f\,(\vec{v}_1, \vec{v}_2) + \frac{2i}{k}\int f^{*}\,(\vec{v}_2, \vec{n})\,\delta f\,(\vec{v}_1, \vec{n})\,d\omega. \qquad (11)$$

The variational principle obtained in such a manner differs essentially from the Kohn variational principle, which was considered in Chapters I and II. If we consider a spherically symmetrical problem and resolve the wave functions and scattering amplitudes in formula (11) by the /114 spherical functions, then we will arrive at Hulthen's common variational principle for a phase.

A distinction from the variational principle by Hulthen for partial waves is obtained only in the presence of inelastic scattering. The formulation of the given variational principle was explained in the paper by Moiseiwitsch (Ref. 58) in a simple case for s-scattering of hydrogen electrons.

If we utilize this variational principle for the numeric calculations and find such approximate functions, for which the functional $K = 0$, then obviously the scattering amplitude in these functions will satisfy automatically the correlation of unitarity.

§21. The Scattering of Electrons by Atoms and the Conditions of Symmetry

We will consider as before, for the sake of substantiality, the collisions of electrons with hydrogen, although the results are generalized directly to more complicated cases.

In order to obtain a formulation of the principle of separate equilibrium for the given problem, we will consider the condition of symmetry

$$I\,(\Psi_1^{(i)}, \Psi_2^{(j)}) = I\,(\Psi_2^{(j)}, \Psi_1^{(i)}), \qquad (1)$$

where the function Ψ satisfies equation (7.1) and has an asymptotic form (8.1) and (8.9), and the functional I is determined by the formula (8.10).

The condition (1) might be put down in the following form

$$\iint [\Psi_1^{(i)}\,(\nabla_1^2 + \nabla_2^2)\,\Psi_2^{(j)} - \Psi_2^{(j)}\,(\nabla_1^2 + \nabla_2^2)\,\Psi_1^{(i)}]\,d\tau_1\,d\tau_2 = 0. \qquad (2)$$

By utilizing Green's formula twice, we obtain

$$\lim_{R_2 \to \infty} \int d\tau_1 \int_{r_2 = R_2} \left[\psi_1^{(i)} \frac{\partial}{\partial r_2} \psi_2^{(j)} - \psi_2^{(j)} \frac{\partial}{\partial r_2} \psi_1^{(i)} \right] dS_2 +$$

$$+ \lim_{R_1 \to \infty} \int d\tau_2 \int_{r_1 = R_1} \left[\psi_1^{(i)} \frac{\partial}{\partial r_1} \psi_2^{(j)} - \psi_2^{(j)} \frac{\partial}{\partial r_1} \psi_1^{(i)} \right] dS_1 = 0. \quad (3)$$

In this formula the asymptotic form of the wave function (8.1) and /115 (8.9) might be substituted. By utilizing the orthogonal and standardized function ψ_n, we arrive in our final calculation toward the surface integral (analyzed in the preceding section). By solving the amplitude f_{ij} by the spherical function and utilizing the addition theorem, we obtain an identity which combines the amplitudes of scattering of the direct and reverse processes

$$\frac{1}{k_j} f_{ij} (\vec{v}_1, \vec{v}_2) = \frac{1}{k_i} f_{ji} (\vec{v}_2, -\vec{v}_1). \quad (4)$$

The equation which combines the differential and fully effective cross sections for the inelastic collisions (8.4) to (8.6) follows directly from this formula (see Landau and Lifshits, Ref. 36, Section 116),

$$k_i^2 \sigma_{ij} (\vec{v}_1, \vec{v}_2) = k_j^2 \sigma_{ji} (-\vec{v}_2, -\vec{v}_1); \quad k_i^2 \sigma_{ij} = k_j^2 \sigma_{ji}. \quad (5)$$

Analogous identities might be obtained also for exchange amplitudes g_{ij}. For instance, from the condition

$$I [\psi_1^{(i)} (\vec{r}_1, \vec{r}_2), \psi_2^{(j)} (\vec{r}_2, \vec{r}_1)] =$$

$$= I [\psi_2^{(j)} (\vec{r}_2, \vec{r}_1), \psi_1^{(i)} (\vec{r}_1, \vec{r}_2)] \quad (6)$$

it is easy to obtain with the same method the equation

$$\frac{1}{k_j} g_{ij} (\vec{v}_1, -\vec{v}_2) = \frac{1}{k_i} g_{ji} (\vec{v}_2, -\vec{v}_1). \quad (7)$$

In order to obtain the second basic identity, the analogous identities (17.10), (18.6) and (19.18) should be based on the condition

$$I\left[\Psi_1^{(i)*}(\vec{r}_1, \vec{r}_2),\ \Psi_2^{(j)}(\vec{r}_1, \vec{r}_2)\right] =$$

$$= I\left[\Psi_2^{(j)}(\vec{r}_1, \vec{r}_2),\ \Psi_1^{(i)*}(\vec{r}_1, \vec{r}_2)\right];$$

$$I\left[\Psi_1^{(i)*}(\vec{r}_1, \vec{r}_2),\ \Psi_2^{(j)}(\vec{r}_2, \vec{r}_1)\right] =$$

$$= I\left[\Psi_2^{(j)}(\vec{r}_2, \vec{r}_1),\ \Psi_1^{(i)*}(\vec{r}_1, \vec{r}_2)\right]; \qquad (8)$$

whereby in the asymptotic form (8.9) of the function Ψ_i, we should exchange ψ_n^* with ψ_n.

By conducting these same calculations we arrive at the following formulae /116

$$\frac{1}{2i}\left[\frac{1}{k_j} f_{ij}^*(\vec{v}_1, \vec{v}_2) - \frac{1}{k_i} f_{ji}(\vec{v}_2, \vec{v}_1)\right] =$$

$$= -\frac{1}{4\pi}\sum_n \frac{1}{k_n}\left[\int f_{in}^*(\vec{v}_1, \vec{n})\, f_{jn}(\vec{v}_2, \vec{n})\, d\omega + \right.$$

$$\left. + \int g_{in}^*(\vec{v}_1, \vec{n})\, g_{jn}(\vec{v}_2, \vec{n})\, d\omega\right]; \qquad (9)$$

$$\frac{1}{2i}\left[\frac{1}{k_j} g_{ij}^*(\vec{v}_1, \vec{v}_2) - \frac{1}{k_i} g_{ji}(\vec{v}_2, \vec{v}_1)\right] =$$

$$= -\frac{1}{4\pi}\sum_n \frac{1}{k_n}\left[\int g_{in}^*(\vec{v}_1, \vec{n})\, f_{jn}(\vec{v}_2, \vec{n})\, d\omega + \right.$$

$$\left. + \int f_{in}^*(\vec{v}_1, \vec{n})\, g_{jn}(\vec{v}_2, \vec{n})\, d\omega\right]. \qquad (10)$$

Thus, the formulae derived in the preceding section can be easily generalized to a problem of two bodies: the collision between an electron and a hydrogen atom.

It can be seen directly from the deriviation of these formulae that they are of the most general character.

If we assume that $i = j$, $\vec{v}_1 = \vec{v}_2$ and, if we utilize formulae (8.4) and (8.6) for the differential and complete effective cross-section, then formula (9) adopts the following form

$$\frac{1}{2ik_i}\left[f_{ii}(\vec{v}, \vec{v}) - f^*_{ii}(\vec{v}, \vec{v})\right] = \frac{k_i}{4\pi}\sigma_i; \qquad (11)$$

$$\operatorname{Im}\left[f_{ii}(\vec{v}, \vec{v})\right] = \frac{k_i^2}{4\pi}\sigma_i; \quad \sigma_{ii}(\vec{v}, \vec{v}) \geq \frac{k_i^2}{16\pi^2}\sigma_i^2,$$

which is analogous to formulae (18.9) and (18.10).

In this section and also in Section 5 we have calculated the surface integrals by the sphere of a large radius, resolving the scattering amplitudes into a row by spherical functions and utilizing the addition theorem.

During the calculation of analogous integrals in Chapter I, we have conducted a direct integration in the derivation of the variacional principles, with the method proposed by Dirac (Ref. 59, p. 205). /117 It is obvious that both methods of calculation are equivalent; the calculations in Chapter I might have been conducted with the same success by using the method utilized in this chapter and vice versa.

§22. Invariance in the Correlation of Unitarity During the Phase Conversion of Atomic Functions

Formula (21.9), derived in the preceding section, would not change its form if we multiplied one of the atomic wave functions ψ_s by the phase multiplier $e^{i\alpha}$. We will prove that this condition is actually accomplished.

In the case of large r_2, the asymptotic form of the function $\psi_1^{(i)}$, $\psi_2^{(j)}$, we know that

$$\psi_1^{(i)} \sim \psi_i(\vec{r}_1)\, e^{ik_i\vec{v}_1\cdot\vec{r}_2} + \sum_n \psi_n f_{in}\frac{e^{ik_n r_2}}{k_n r_2}; \qquad (1)$$

$$\Psi_2^{(j)} \sim \psi_j(\vec{r}_1)\, e^{ik_j \vec{r}_2 \cdot \vec{r}_2} + \sum_n \psi_n f_{jn} \frac{e^{ik_n r_2}}{k_n r_2}. \qquad (2)$$

We will consider a most simple case; when the function ψ_s is exchanged

$$\tilde{\psi}_s = \psi_s e^{i\alpha}, \qquad (3)$$

whereby $i \neq s$, $j \neq s$. The remaining function ψ_n will remain unchanged. During such an exchange the scattering amplitudes f_{is}, f_{js} should change in such a manner that the functions $\Psi_1^{(i)}$ and $\Psi_2^{(j)}$ would not be subjected to any change. It is obvious that

$$\tilde{f}_{is} = e^{-i\alpha} f_{is}; \quad \tilde{f}_{js} = e^{-i\alpha} f_{js}. \qquad (4)$$

All remairing amplitudes f_{mn} will thereby remain unchangeable. If we substitute $\tilde{f}_{is}$ and $\tilde{f}_{js}$ in formula (21.9) in place of f_{is} and f_{js}, the phase multipliers would become condensed in the s-term, and the formula would remain unchangeable. This same effect will also be obtained in the case of the exchange amplitudes g_{mn}.

We will now assume that $s = i$. Then, by substituting ψ with $\tilde{\psi}_i$, the entire function $\Psi_1^{(i)}$ will be multiplied by the phase multiplier /118 $e^{i\alpha}$; consequently, each one of the amplitudes f_{in} will thereby be substituted as follows

$$\tilde{f}_{in} = e^{i\alpha} f_{in}, \qquad (5)$$

with the exception of f_{ii}, which will remain unchanged. In the function $\Psi_2^{(j)}$ only the amplitude f_{ji} will, as before, be exchanged

$$\tilde{f}_{ji} = f_{ji} e^{-i\alpha}. \qquad (6)$$

We will write down equation (21.9) disregarding the exchange amplitudes

$$\frac{1}{2i}\left[\frac{1}{k_j} f_{ij} - \frac{1}{k_i} f^*_{ji}\right] = \frac{1}{4\pi}\sum_n \frac{1}{k_n} \int f_{in} f^*_{jn}\, d\omega. \qquad (7)$$

We will multiply all equalities by $e^{i\alpha}$ and we will record separately the term of the sum with n = i

$$\frac{1}{2i}\left[\frac{1}{k_j}(f_{ij}e^{i\alpha}) - \frac{1}{k_i}(f_{ji}e^{-i\alpha})^*\right] =$$

$$= \frac{1}{4\pi}\left[\sum_{n\neq i} \frac{1}{k_n}\int (f_{in}e^{i\alpha})\, f^*_{jn}\, d\omega + \frac{1}{k_i}\int f_{ii}\,(f_{ji}e^{-i\alpha})^*\, d\omega\right]. \qquad (8)$$

By utilizing formulae (5) and (6), we obtain

$$\frac{1}{2i}\left[\frac{1}{k_i}\tilde{f}_{ij} - \frac{1}{k_j}\tilde{f}^*_{ji}\right] = \frac{1}{4\pi}\sum_n \frac{1}{k_n}\int \tilde{f}_{in}\,\tilde{f}^*_{jn}\, d\omega. \qquad (9)$$

If we take into consideration amplitudes g_{mn}, then all reasonings will undergo an essential change.

Thus, the invariance of equation (21.9) is proved. A generalization of the obtained results, in the case of several functions ψ_n being multiplied simultaneously by the phase multiplier $e^{i\alpha_n}$, is trivial. This proof can also easily be made in the case of formula (21.10).

§23. The Correlation of Unitarity and the Relation Between the Elastic and Inelastic Partial Effective Cross Sections of Scattering

/119

During the deriviation of equations (21.9) and (21.10) it was not required, generally speaking, that the energy operator possess a spherical symmetry. If we should make such an assumption and, in addition, assume also that i = j, then after the solution of the amplitudes f_{ij} and g_{ij} by the Legendre polynomials, we will obtain a correlation which would bind

the amplitude of the falling and scattered partial waves. This correlation expresses the preservation of the number of particles and might be obtained also from the conversion into 0 of the complete current through the sphere of a large radius surrounding the atom (see, for example, the paper by G. F. Drukarev, Ref. 54), in the same manner as was done in Section 17 for a very simple problem. Actually

$$f_{in} = \sum_{\ell=0}^{\infty} c_{in}^{(\ell)} P_\ell (\vec{v} \cdot \vec{n}), \tag{1}$$

$$g_{in} = \sum_{\ell=0}^{\infty} d_{in}^{(\ell)} P_\ell (\vec{v} \cdot \vec{n}). \tag{2}$$

Then, we obtain, for the respective effective cross sections

$$\sigma_{in} = \frac{1}{k_i k_n} \int |f_{in} (\vec{v} \cdot \vec{n})|^2 \, d\omega =$$

$$= \frac{1}{k_i k_n} \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell + 1} |c_{in}^{(\ell)}|^2 = \sum_{\ell=0}^{\infty} \sigma_{in}^{(\ell)}, \tag{3}$$

where $\sigma_{in}^{(\ell)}$ are the partial effective cross sections of the non-interchangeable scattering. In an analogous manner the partial cross section of an interchangeable scattering can be determined.

If we should substitute solutions (1) and (2) in formula (21.9). assuming thereby that i = j, and if we should utilize the addition theorem, then we will obtain /120

$$\sum_{\ell=0}^{\infty} \frac{1}{2ik_i} (c_{ii}^{(\ell)} - c_{ii}^{(\ell)*}) P_\ell (\vec{v}_1 \cdot \vec{v}_2) =$$

$$= \frac{1}{4\pi} \sum_n \frac{1}{k_n} \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell + 1} (|c_{in}^{(\ell)}|^2 + |d_{in}^{(\ell)}|^2) P_\ell (\vec{v}_1 \cdot \vec{v}_2). \tag{4}$$

By comparing the coefficients at identical Legendre polynomials, we have

$$\frac{1}{2i}\left(c_{ii}^{(\ell)} - c_{ii}^{(\ell)*}\right) = \frac{k_i^2}{4\pi}\sum_n \sigma_{in}^{(\ell)} = \frac{k_i^2}{4\pi}\sigma_i^{(\ell)} \quad \frac{k_i^2}{4\pi}\left(\sigma_{ie}^{(\ell)} + \sigma_{ia}^{(\ell)}\right). \tag{5}$$

In this case $\sigma_i^{(\ell)}$, $\sigma_{ie}^{(\ell)}$, $\sigma_{ia}^{(\ell)}$ are, respectively, complete, elastic and inelastic partially effective cross sections, whereby the number of inelastic processes includes also the elastic scattering exchange. Let us assume that $c_{ii}^{(\ell)} = \rho e^{i\varnothing}$. Then

$$\sigma_{ie}^{(\ell)} = \frac{4\pi\rho^2}{k_i^2\,(2\ell+1)} = \rho^2\sigma_{i0}^{(\ell)}, \quad \sigma_{i0}^{(\ell)} = \frac{4\pi}{k_i^2\,(2\ell+1)} \tag{6}$$

and formula (5) might be recorded as

$$\sigma_{ia}^{(\ell)} = \sqrt{\sigma_{i0}^{(\ell)}\sigma_{ie}^{(\ell)}}\,\sin\varnothing - \sigma_{ie}^{(\ell)}. \tag{7}$$

$\sigma_{ia}^{(\ell)}$ can not be less than 0. From this follows

$$\sigma_{ie}^{(\ell)} \leq \sigma_{i0}^{(\ell)}, \tag{8}$$

i.e., the corss section $\sigma_{i0}^{(\ell)}$ is the largest possible partial cross section of elastic scattering. At a given value $\sigma_{ie}^{(\ell)}$ the possible values $\sigma_{ia}^{(\ell)}$ are limited by the inequality

$$0 \leq \frac{\sigma_{ia}^{(\ell)}}{\sigma_{i0}^{(\ell)}} \leq \sqrt{\frac{\sigma_{ie}^{(\ell)}}{\sigma_{i0}^{(\ell)}} - \frac{\sigma_{ie}^{(\ell)}}{\sigma_{i0}^{(\ell)}}}. \tag{9}$$

In Fig. 2 the possible joint values $\sigma_{ie}^{(\ell)}$ and $\sigma_{ia}^{(\ell)}$ are defined/121 by the shaded region. An analogous graph is available in the book by Blatt and Weiskopf (Ref. 60, p. 255). The curve in this graph represents a parabola with its apex at the point $\left(\frac{1}{16}\sigma_{i0}^{(\ell)}, \frac{3}{16}\sigma_{i0}^{(\ell)}\right)$.

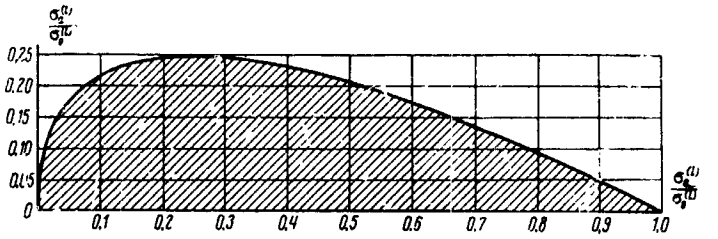

Fig. 2. Possible Joint Values of the Relation of Elastic ($\sigma_e^{(\ell)}$) and Inelastic ($\sigma_a^{(\ell)}$) Partially Effective Cross-Sections Toward the Specific Cross-Section $\sigma_0^{(\ell)} \frac{4\pi}{k^2 (2\ell + 2)}$.

The result obtained is general and true if a solution by partial waves is possible; that is, if the operator of energy commutates with the operator of the amount of motion moment.

§24. The Principle of Reversibility in Quantum Mechanics

It is a well known fact that the principle of separate equilibrium or the principle of reversibility is fulfilled in quantum mechanics. It is confirmed that the probability of transition of a system from state A into state B and from state B into state A should equal each other. In classical mechanics this assertion can be easily obtained from the fact that in a conservative force field a particle might travel along a trajectory in straight as well as reverse directions. It is possible to prove that when this rule is not carried out (for instance, in the case of motion of charged particles in a magnetic field) the principle of reversibility is not damaged.

Another basic situation for proving the principle of separate/122 equilibrium in classical mechanics is the Liouville theorem from which it follows that density in a phase space does not change during an exchange of systems in time.

The principle of separate equilibrium finds an important application in statistical physics and is closely related to the second principle of thermo dynamics.

In quantum mechanics it is possible to establish (by utilizing the separate equilibrium principle) the relations between direct and reverse processes in the theory of collisions; between a quasi-stationary state and scattering (Breit-Wigner resonance formula); between scattering of particles which fall on a potential barrier from the right and the left sides, etc.

Therefore, it is essential to give a general rule for the derivation of the separate equilibrium principle from a quantum mechanical standpoint. It is commonly asserted (see, for instance, Ref. 36), that this principle follows from the invariance of the Schroedinger equation regarding the exchange of ψ with ψ^* and t with -t.

However, this reasoning is not convincing, since the wave function $\psi^* (x, -t)$ does not characterize the reverse process at all and, as a rule, does not have any simple physical sense. For instance, in a problem on the scattering of particles by a potential field, the wave function $\Psi^* (\vec{r}, -t)$ will have the following asymptotic form in the presence of large r

$$\Psi^* (\vec{r}, -t) \sim e^{ik\vec{v}\cdot\vec{r}-iEt} + f^* (\vec{v}, \vec{n}) \frac{e^{-ikr - iE\ell}}{kr}, \qquad (1)$$

that is, we can see that in the case of large r the function $\Psi^* (\vec{r}, -t)$ is represented by the imposition of converging spherical and flat waves. This function will, of course, satisfy the Schroedinger equation; however, from this fact does not follow at all for instance the equation

$$f (\vec{v}_1, \vec{v}_2) = f (-\vec{v}_2, -\vec{v}_1) \qquad (2)$$

which was derived in Section 19, and which expresses the principle of separate equilibrium. The sense of the wave function which was reversed into the past, differs essentially from its normal sense. This problem was investigated by V. A. Fok (Ref. 61). /123

The equality (2) was derived, for instance, in the paper (Ref. 62) by a strict but sufficiently complicated method. Formulae (2) and (21.4) can be easily obtained within the frameworks of the Born approximation; however, the transition from the Born approximation toward a general case does not represent a trivial task.

On the basis of the results obtained in Sections 1 through 5 of this chapter, we might assert that for a wide range of problems in the collision theory and also, for instance, in the case of problems on the passage of particles through a potential barrier, the principle of separate equilibrium follows from the symmetry of the functional

$$I(\Psi_2, \Psi_1) = \int \Psi_2 (H - E) \Psi_1 d\tau \tag{3}$$

in regard to the displacement of the functions Ψ_1 and Ψ_2 which characterize the intial and final states.

In the separate equilibrium principle, we will examine the passage of a system between two states: A and B. However, in collision theory the stationary problem concerning the scattering of a flat wave is solved and, therefore, no passage or change in time with the system occurs. In order to clarify the way in which the idea of transitions between two states is related to our stationarity of the wave function, it is first of all necessary to accurately determine the state of the system.

In the problem concerning the collision of an electron with an atom the state of the system is known if we measure the impulse of the free electron and the state of the atom which is determined by a certain collection of quantum numbers. Such a determination of state is the most natural. The wave function which characterizes this state of the system will have the form

$$e^{i\vec{k}\cdot\vec{r}_0} \psi(\vec{r}_1, \cdots, \vec{r}_n), \tag{4}$$

where $\vec{k}$ is the impulse (the wave vector) of the free electron and ψ is the wave function of the atom.

The energy operator H_0 to which these functions will belong is obtained from the total energy operator H minus that portion which /124 corresponds to the interaction of the atom with a free electron. (Let us note that, while considering the exchange this part can be different for the initial and final states). Thus, we come to the usual organization of the problem: under the influence of excitation the system passes from one state into another. Analogous to the way this was done in Section 17, the stationary wave function can be represented as a result of a certain limitary passage from a non-stationary wave function. (The possibility of this limitary passage was shown for example in Ref. 27). Then the scattering amplitude f_{AB} will actually characterize the probability of the transition of the system from one state into another.

We will note a certain difference between the scattering amplitudes for a reverse process in formula (21.4) and formulae (21.9), (21.10).

The initial state A is characterized by the wave function

$$\Psi_A = e^{ik_i \vec{v}_1 \cdot \vec{r}_2} \psi_i(\vec{r}_1), \tag{5}$$

and the final state B by the function

$$\Psi_B = e^{ik_j \vec{v}_2 \cdot \vec{r}_2} \psi_j(\vec{r}_1). \tag{6}$$

The passage between these two states is characterized by the scattering amplitude

$$f_{AB} = f_{ij}(\vec{v}_1, \vec{v}_2). \tag{7}$$

f_{AB} is compared in the principle of separate equilibrium with amplitude $f_{B^*A^*}$ of the passage between states B*

$$\Psi_{B^*} = e^{-ik\vec{v}_2 \cdot \vec{r}_2} \psi_j^*(\vec{r}_1) = \Psi_B \tag{8}$$

and A*

$$\Psi_{A^*} = e^{-ik\vec{v}_1 \cdot \vec{r}_2} \psi_i^*(\vec{r}_1) = \Psi_A^* \tag{9}$$

The form of the function Ψ_{B^*}, Ψ_{A^*} follows directly from the asymptotic form of the function $\Psi_1^{(i)}$, $\Psi_2^{(j)}$. /125

In formula (21.9) the amplitude $f_{ji}(\vec{v}_2, \vec{v}_1)$ of the reverse process characterizes the passage between the states of B and A with functions (6) and (5).

Thus, in formula (21.9) f_{ji} actually characterizes the reverse passage and in formula (21.4) f_{ji} characterizes the reverse passage between the complex conjugate states. By discarding the weight factors we can write down equations (21.4), (21.9) for the general problem of collision theory as follows

$$f_{AB} = f_{B^*A^*}, \tag{10}$$

$$\frac{1}{2i}(f_{AB} - f^*_{BA}) = \sum_C f_{AC} f^*_{BC}. \tag{11}$$

Here the summation is extended to all states C of the system which are possible at the given energy value.

During calculation of the scattering amplitudes by the Born method, we consider all f small and we neglect the magnitudes of the second order. Therefore, in the first Born approximation, we neglect the right part of equation (1), and we obtain

$$f_{AB} - f^*_{BA} = 0. \tag{12}$$

However, in the second approximation of the excitation theory this difference will not be 0.

If the scattering matrix S is formed according to the formula

$$S_{AB} = \delta_{AB} - 2i f_{AB}, \tag{13}$$

then equations (10), (11) will be written in the form

$$S_{AB} = S_{B^*A^*}, \quad \sum_C S^*_{AC} S_{BC} = \delta_{AC}, \tag{14}$$

i.e., they express the condition of symmetry and unitarity of the matrix S.

§25. The Symmetry of the Functional and Variational Principle for the Non-Stationary Problem /126

We will examine the non-stationary quantum mechanics problem. The Schroedinger equation in this case has the form

$$H\Psi = i\frac{\partial \Psi}{\partial t}. \tag{1}$$

We will limit ourselves to a case where the energy operator H is not dependent on time. We will thereby consider that operator H might even be non-self conjugated. This means that we include in the consideration also such processes in which a number of particles is not preserved with time and consequently the standard integral $\int |\Psi|^2 \, d\tau$ is dependent on time.

We will examine the probability of transition of the system from some initial state, the moment t_1, into a certain final state, the moment t_2. To do this we shall introduce two self conjugated operators A and B with their functions u_i and v_j

$$Au_i = \alpha_i u_i, \tag{2}$$

$$Bv_j = \beta_j v_j \tag{3}$$

and we shall consider that a task of the value of α_i or β_j simply determines the state of the system.*

That the function Ψ in the initial moment $t_1 = u_i$

$$\Psi_1^{(i)}(t_1) = u_i. \tag{4}$$

It is required to determine the probability of the fact that at the moment t_2, the system will be in the state v_j. It is obvious that this probability will equal the square of the modulus of magnitude

$$S_{A_i B_j}(t_1, t_2) = \int v_j^* \Psi_1^{(i)}(t_2) \, d\tau, \tag{5}$$

which we will call the matrix of transition.

We will examine the specific function of the operators H and H^+ /127

$$H\psi_n = E_n \psi_n, \tag{6}$$

*In a majority of cases the condition of the system is simply determined if the values are set up, not for one, but for several operators. However, in principle, this does not change the operation.

$$H^{+} \varphi_n = E_n^{*} \varphi_n, \tag{7}$$

which satisfies the condition of orthogonality

$$\int \varphi_m^{*} \psi_n \, d\tau = \delta_{mn}. \tag{8}$$

We shall arrange in a row through these functions u_i and v_j

$$u_i = \sum_n a_{in} \psi_n = \sum_n a_{in}^{(+)} \varphi_n, \tag{9}$$

$$v_j = \sum_n b_{jn}^{(+)} \varphi_n = \sum_n b_{jn} \psi_n. \tag{10}$$

Then the function $\Psi_1^{(i)}$ can be presented in the form

$$\Psi_1^{(i)} = \sum_n a_{in} \psi_n e^{-iE_n(t - t_1)}, \tag{11}$$

and the matrix of transition S will be equal to

$$S_{A_i B_j}(t_1, t_2) = \sum_n b_{jn}^{(+)*} a_{in} e^{-iE_n (t_2 - t_1)}. \tag{12}$$

We will formulate the separate equilibrium principle for this general problem. To do this, we will examine the equation

$$H'\Phi = i \frac{\partial \Phi}{\partial t}, \quad H' = (H^{+})^{*}, \tag{13}$$

where H' is the transposed energy operator H, and we will determine the probability of transition on the state v_j^{*}, the moment t_1, into the state u_i^{*}, the moment t_2. Then the initial condition for the function Φ will have the form

$$\Phi_1^{(j)}(t_1) = v_j^*, \tag{14}$$

and the magnitude which must be determined will be equal to

$$S^{(')}_{B_j A_i^*} = \int u_i \Phi_1^{(j)}(t_2)\, d\tau. \tag{15}$$

Operator H' has the same specific values as operator H /128

$$H'\varphi_n^* = E_n \varphi_n^*. \tag{16}$$

By resolving $\Psi_1^{(j)}$ through the functions φ_n^*, we obtain

$$\Phi_1^{(j)} = \sum_n b_{jn}^{(+)*} \varphi_n^* e^{-iE_n (t - t_1)}; \tag{17}$$

$$S^{(')} = \sum_n a_{in} b_{jn}^{(+)*} e^{-iE_n (t_2 - t_1)}. \tag{18}$$

Thus

$$S^{(')}_{B_j * A_i *}(t_1, t_2) = S_{A_i B_j}(t_1, t_2). \tag{19}$$

Hence, the matrix elements of transition from the state u, the moment t_1 into the state v, the moment t_2 (the energy operator H) and the transition from state v^*, the moment t_1 into the state u^*, the moment t_2 (the energy operator H') are reciprocally equal.

In order to obtain a correlation analogous to the correlation of unitarity, we introduce, apart from the operators A and B, a third operator C with a specific function w_k

$$w_k = \sum_n C_{kn} \psi_n; \quad w_k = \sum_n C^{(+)}_{kn} \varphi_n. \tag{20}$$

then the matrix of transition from state v_j, the moment t_2 into the state w_k, the moment t_3 will have the form

$$S_{B_j C_k}(t_2, t_3) = \sum_m C^{(+)*}_{km} b_{jm} e^{-iE_m (t_3 - t_2)}. \tag{21}$$

By utilizing the correlation

$$\sum_j b^{(+)*}_{jn} b_{jm} = \int \varphi^*_n \psi_m \, d\tau = \delta_{nm} \tag{22}$$

and the expression for the matrices of transition (12) and (21), we obtain the correlation

$$\sum_j S_{A_i B_j}(t_1, t_2) S_{B_j C_k}(t_2, t_3) = S_{A_i C_k}(t_1, t_3). \tag{23}$$

Thus, the matrix element of transition from the initial into a final state can be obtained by means of a summation through the intermediate state. By letting $C = A$ and $t_3 = t_1$, we will obtain the correlations which are analogous to the correlations of the unitarity introduced in the preceding sections. /129

We will now formulate a variational principle for the observed non-stationary problem. Hereby, for simplicity we will let $H^+ = H$ although such an assumption is not compulsory.

We will form the functional

$$I(\Psi^{(j)}_2, \Psi^{(i)}_1) = \int_{t_1}^{t_2} dt \int \Psi^{(j)*}_2 \left(H - i \frac{\partial}{\partial t}\right) \Psi^{(i)}_1 \, d\tau, \tag{24}$$

in which the functions $\tilde{\Psi}_1^{(i)}$, $\tilde{\Psi}_2^{(j)}$ satisfy the conditions

$$\tilde{\Psi}_1^{(i)}(t_1) = u_i, \quad \tilde{\Psi}_2^{(j)}(t_2) = v_j, \tag{25}$$

and we shall examine the variation of this functional in the neighborhood of the functions $\Psi_1^{(i)}$, $\Psi_2^{(j)}$ which are accurate solutions to equation (1) with the initial conditions (25). Then, through an analysis of the functions Ψ and $\tilde{\Psi} = \Psi + \delta\Psi$ by the specific functions of the operator H, we obtain

$$\Psi_1^{(i)} = \sum_n a_{in}\psi_n e^{-iE_n(t - t_1)}, \tag{26}$$

$$\Psi_2^{(j)} = \sum_n b_{jn}\psi_n e^{-iE_n(t - t_2)}, \tag{27}$$

$$\tilde{\Psi}_1^{(i)} = \Psi_1^{(i)} + \delta\Psi_1^{(i)} = \sum_n (a_{in} + \delta a_{in})\,\psi_n e^{-iE_n(t-t_1)}, \tag{28}$$

$$\tilde{\Psi}_2^{(j)} = \Psi_2^{(j)} + \delta\Psi_2^{(j)} = \sum_n (b_{jn} + \delta b_{jn})\,\psi_n e^{-iE_n(t-t_2)}. \tag{29}$$

Here, the coefficients a_{in}, b_{jn} are not dependent upon time and δa_{in}, δb_{jn} are the functions of time and satisfy the conditions

$$\delta a_{in}(t_1) = 0, \tag{30}$$

$$\delta b_{jn}(t_2) = 0. \tag{31}$$

By substituting expressions (28) and (29) for functions $\tilde{\Psi}_1^{(i)}$, $\tilde{\Psi}_2^{(j)}$ in the functional (24), we obtain /130

$$I(\tilde{\Psi}_2^{(j)}, \tilde{\Psi}_1^{(i)}) = I(\Psi_2^{(j)}, \Psi_1^{(i)}) + \delta I = \delta I =$$

$$= \sum_n \int_{t_1}^{t_2} b_{jn}^* e^{iE_n(t-t_2)} \left(E_n - i\frac{\partial}{\partial t}\right) \delta a_{in} e^{-iE_n(t-t_1)} dt +$$

$$+ \int_{t_1}^{t_2} dt \int \delta\Psi_2^{(j)*} \left(H - i\frac{\partial}{\partial t}\right) \delta\Psi_1^{(i)} d\tau. \qquad (32)$$

By conducting an integration through the parts in the first integral and taking into consideration condition (30), we obtain

$$\delta I = -i \sum_n b_{jn}^* \delta a_{in}(t_2) e^{-iE_n(t_2-t_1)} +$$

$$+ \int_{t_1}^{t_2} dt \int \delta\Psi_2^{(j)*} \left(H - i\frac{\partial}{\partial t}\right) \delta\Psi_1^{(i)} d\tau. \qquad (33)$$

It is easily convincing that the first member of this expression coincides accurately up to the factor with a variation of the matrix element of transit $S_{A_iB_j}(t_1, t_2)$.

Actually

$$\tilde{S}_{A_iB_j}(t_1, t_2) = \int v_j^* \tilde{\Psi}_1^{(i)}(t_2) d\tau =$$

$$= \sum_n b_{jn}^* [a_{in} + \delta a_{in}(t_2)] e^{-iE_n(t_2-t_1)} =$$

$$= S_{A_iB_j}(t_1, t_2) + \delta S_{A_iB_j}(t_1, t_2). \qquad (34)$$

By disregarding the members of the second order, we obtain

$$\delta I = - i\delta S_{A_i B_j} (t_1, t_2). \tag{35}$$

Thus, the stationary value of the functional

$$J(\tilde{\Psi}_2^{(j)}, \tilde{\Psi}_1^{(i)}) = \tilde{S}_{A_i B_j} (t_1, t_2) + \frac{1}{i} (\tilde{\Psi}_2^{(j)}, \tilde{\Psi}_1^{(i)}) =$$

$$= \int v_j^* \tilde{\Psi}_1^{(i)} (t_2)\, d\tau + \frac{1}{i} \int_{t_1}^{t_2} dt \int \tilde{\Psi}_2^{(j)*} \left(H - i \frac{\partial}{\partial t}\right) \tilde{\Psi}_1^{(i)}\, d\tau, \tag{36}$$

under additional conditions (25) is equal to the matrix element of transition $S_{A_i B_j}$: /131

$$S_{A_i B_j} (t_1, t_2) = St\, J(\tilde{\Psi}_2^{(j)}, \tilde{\Psi}_1^{(i)}). \tag{37}$$

By utilizing the obtained variational principle we can work out the approximate methods of calculation of transition probabilities and likewise derive other results which were obtained in Chapter II for the stationary problems. Thus, for example, by substituting instead of function $\tilde{\Psi}_1^{(i)}$ the function u_i, and instead of function $\tilde{\Psi}_2^{(j)}$ the accurate function $\Psi_2^{(j)}$, we obtain also an expression for the matrix element of transition, which is analogous to the integral identity derived in Section 10:

$$S_{A_i B_j} (t_1, t_2) = \int v_j^* u_i\, d\tau + \frac{1}{i} \int_{t_1}^{t_2} dt \int \Psi_2^{(j)*} H u_i\, d\tau. \tag{38}$$

The extreme transition from non-stationary to stationary problems is concluded first of all in the fact that the initial and final moments of time, respectively, approach $-\infty$ and $+\infty$. In addition, for the scattering problem, operators A and B in this case characterize the direction of movement, the velocity, and the interstate of the colliding particles, respectively, before and after collision.

Within its limit the wave function Ψ_1 produces a function which satisfies the radiation principle, the asymptotic form of which contains plain and divergent waves; the function Ψ_2 satisfies within its limit the reverse radiation principle. As t_1 and t_2 approach $\pm\infty$ within the limit, all matrix elements for the transitions with an energy change of the system, are reduced to zero.

The correlation which relates the complete cross section of scattering with the imaginary part of the scattering amplitude on a zero angle was obtained in the case of the quantum mechanics problem by Feenberg (Ref. 63) and was considered further in a series of works (Ref. 64). In a general form the symmetry properties of the scattering matrix were investigated in the work by Lippman and Schwinger (Ref. 27). The general properties of the matrix of transition, which were examined in this section, are analogous to the initial correlations in the work (Ref. 65). The derivation of the characteristics of symmetry for /132 stationary problems examined in this chapter is present in the author's work (Ref. 66). In Ref. 67 the correlation of unitarity is utilized for an estimation of the imaginary part of the elastic scattering amplitude of the electrons by atoms. The results obtained are utilized for the interpretation of experiments in electron difraction on molecules.

The formulation of a variational principle for non-stationary problems when the energy operator is likewise dependent on time is present in the work (Ref. 68).

CHAPTER IV

/133

THE VARIATION OF SCALE AND THE VIRIAL THEOREM FOR PROBLEMS OF SCATTERING

§26. The Virial Theorem in Classical Mechanics

We will examine the system with n degrees of freedom which is described by the Lagrange function $L(q_1, q_2, \cdots, q_n; \dot{q}_1, \dot{q}_2, \cdots, \dot{q}_n)$ and is not dependent on time, and we shall proceed from the Hamilton variational principle. According to this principle, the integral

$$S = \int_{t_1}^{t_2} L\,(q_1, \cdots, q_n;\ \dot{q}_1, \cdots, \dot{q}_n)\,dt, \tag{1}$$

which is calculated along the true path is stationary relative to any given variation of generalized coordinates q_i (t) in the case where the variations δq_i (t) are reduced to 0 when $t = t_1$ and $t = t_2$. If this condition is not observed, then

$$\delta S = \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i}\,\delta q_i \Bigg|_{t=t_1}^{t=t_2}. \tag{2}$$

We shall vary the scale; that is, we shall let $\delta q_i = \epsilon q_i(t)$ where ϵ is the small parameter. Then, by disregarding the members which are proportional to ϵ^2, we have

$$S + \delta S = \int_{t_1}^{t_2} L\,(q_1 + \epsilon q_1, \cdots, q_n + \epsilon q_n;\ \dot{q}_1 + \epsilon\dot{q}_1, \cdots, \dot{q}_n + \epsilon\dot{q}_n)\,dt =$$

$$= \int_{t_1}^{t_2} L\,(q_1, \cdots, q_n;\ \dot{q}_1, \cdots, \dot{q}_n)\,dt +$$

$$+ \epsilon \int_{t_1}^{t_2} \sum_{i=1}^{n} \left(\frac{\partial L}{\partial q_i} q_i + \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right) dt. \tag{3}$$

On the other hand according to (2) /134

$$\delta S = \epsilon \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i} q_i \Bigg|_{t_1}^{t_2}. \tag{4}$$

Thus

$$\int_{t_1}^{t_2} \sum_{i=1}^{n} \left(\frac{\partial L}{\partial q_i} q_i + \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right) dt = \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i} q_i \Bigg|_{t_1}^{t_2}. \tag{5}$$

If the movement of the system is periodic than the period T can be taken as a time interval. Then the right member of the equation disappears. If, during an unlimited increase in the interval $t_2 - t_1$, the coordinates and impulses remain limited, then by dividing the equation $t_2 - t_1$ and reaching the limit, we shall again obtain the fact that the right member in the limit is reduced to 0. In both cases

$$\overline{\sum_{i=1}^{n} \left(\frac{\partial L}{\partial q_i} q_i + \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right)} = 0, \tag{6}$$

where the line designates the average in time. For the system N of interacting particles in the potential field

$$L = \sum_{k=1}^{N} \frac{m_k v_k^2}{2} - U(\vec{r}_1, \cdots \vec{r}_N). \tag{7}$$

Equation (6) will be written then as follows

$$\sum_{k=1}^{N} \overline{\left[m_k v_k^2 - \vec{r}_k \cdot \nabla_k U (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \right]} =$$

$$= 2\overline{T} - \sum_{k=1}^{N} \overline{\vec{r}_k \cdot \nabla_k U} = 0. \tag{8}$$

If U is the homogeneous function of the coordinates, i.e., if

$$U (\alpha \vec{r}_1, \alpha \vec{r}_2, \cdots, \alpha \vec{r}_N) = \alpha^m U (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N), \tag{9}$$

where m is the order of homogeneity and according to the Euler theorem on homogeneous functions, we have

$$\sum_{k=1}^{N} \vec{r}_k \cdot \nabla_k U (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = mU. \tag{10}$$

Herefrom and from (8), we obtain /135

$$2\overline{T} = m \overline{U}. \tag{11}$$

In the extremely important, specific case m = - 1 (the movement of charged particles or heavenly bodies)

$$2\overline{T} = - \overline{U}. \tag{12}$$

By utilizing the equation T + U = E which is fulfilled at any given moment of time (7) can be written in another form:

$$\overline{2U} + \sum_{k=1}^{N} \overline{\vec{r}_k \cdot \nabla_k U} = 2E. \tag{13}$$

Formulae (5), (7), (9), (11), (12), and (13) compose the content of the virial theorem in classical mechanics. These formulae are valid only in the case of limited trajectories in the phase space. The virial theorem was originally proved by Clausius and found broad application in

theoretical mechanics as well as in statistical physics. Its derivation from the variational principle was proposed by V. A. Fok and Yu. A. Krutkov (Ref. 69).

§27. The Virial Theorem in Quantum Mechanics. The Related States

We shall consider for simplicity the movement of one particle in a potential well. In this case the energy operator has the form

$$H = -\frac{1}{2}\nabla^2 + U(\vec{r}). \tag{1}$$

In exactly the same way as in classic mechanics, we will proceed from the variational principle for a discrete spectrum.

If the equation

$$H\psi = E\psi \tag{2}$$

has a solution for discrete energy values then the functional

$$\overline{E} = \int \psi^* H\psi \, d\tau \tag{3}$$

under an additional condition /136

$$\int \psi^* \psi \, d\tau = 1 \tag{4}$$

a stationary relative to the arbitrary variation of the function ψ.

We will vary the scale of length in the wave function; i.e., we shall substitute

$$\psi(\vec{r}) \text{ for } \psi(\vec{r} + \epsilon\vec{r}) \tag{5}$$

in the function. In order to satisfy the condition of standardization it is necessary hereby to multiply $\psi(\vec{r} + \epsilon\vec{r})$ by a certain factor. Actually

$$\int \psi^* (\vec{r} + \epsilon\vec{r}) \psi (\vec{r} + \epsilon\vec{r}) d\tau =$$

$$= \int |\psi (\vec{\rho})|^2 d\tau_\rho \cdot \frac{1}{(1+\epsilon)^3} = \frac{1}{(1+\epsilon)^3} . \quad (6)$$

Thus

$$\tilde{\psi} = \psi (\vec{r}) + \delta\psi (\vec{r}) = (1+\epsilon)^{\frac{3}{2}} \psi (\vec{r} + \epsilon\vec{r}) . \quad (7)$$

By substituting the varied function in the functional (3), we have

$$\bar{E} + \delta\bar{E} = (1+\epsilon)^3 \int \psi^* (\vec{r} + \epsilon\vec{r}) \times$$

$$\times \left(-\frac{1}{2} \nabla^2 + U (\vec{r}) \right) \psi (\vec{r} + \epsilon\vec{r}) d\tau =$$

$$= \int \psi^* (\vec{\rho}) \left[-\frac{1}{2} (1+\epsilon)^2 \nabla_\rho^2 + U \left(\frac{\rho}{1+\epsilon} \right) \right] \psi (\vec{\rho}) d\tau_\rho . \quad (8)$$

We shall resolve the right member in degrees of ϵ and we shall discard the members on the order of ϵ^2, ϵ^3, etc.

$$\bar{E} + \delta\bar{E} = \int \psi^* (\vec{\rho}) \left[-\frac{1}{2} \nabla_\rho^2 - \epsilon\nabla_\rho^2 + U (\vec{\rho}) - \epsilon\rho \cdot \nabla_\rho U (\vec{\rho}) \right] \times$$

$$\times \psi (\vec{\rho}) d\tau_\rho = \bar{E} - \epsilon \int \psi^* (\vec{\rho}) [\nabla_\rho^2 + \vec{\rho} \cdot \nabla_\rho U (\vec{\rho})] \psi (\vec{\rho}) d\tau_\rho . \quad (9)$$

From the variational principle it follows that if ψ satisfies /137
equation (2) then the member which is proportional to ϵ should disappear; that is

$$\int \psi^* (\vec{r}) [\nabla^2 + \vec{r} \cdot \nabla U (\vec{r})] \psi (\vec{r}) d\tau = 0. \quad (10)$$

or else

$$2\bar{T} = \overline{\vec{r} \cdot \nabla U (\vec{r})} . \quad (11)$$

By utilizing (2) it is possible to rewrite equation (10) in the form

$$\int |\psi(\vec{r})|^2 [2U(\vec{r}) + \vec{r} \cdot \nabla U(\vec{r})] d\tau = 2E. \quad (12)$$

It is definitely obvious that this derivation is valid also for any given number of particles if by $\vec{r}$ we understand the radius-vector in the space of the configuration. Thus, we will obtain the formulae which are definitely analogous to the formulae of classical mechanics except for the fact that there the average is conducted through a great interval of time and here equation (11) is fulfilled at any given moment t. In exactly this way it is possible to write $2\bar{T} = m\bar{U}$ for a homogeneous function U, and $2\bar{T} = -\bar{U}$ for the Coulomb interation (an atom with many electrons).

The virial theorem in the form (11) was given evidence almost immediately after the creation of quantum mechanics by somewhat more complicated means (Ref. 70). Derivation of this theorem from the variational principle by means of the variation of scale of length was at first proposed by V. A. Fok (Ref. 10). Such a deduction is easily generalized also for a case of the Dirac (Ref. 10) theory and for the Thomas-Fermi (Ref. 71) statistical atom theory.

The method of scale variation was utilized earlier in connection with the Ritz method in variational calculations of energy levels of the simplest atoms for instance by Hylleraas (Ref. 5) for helium and for ions which resemble helium. The scalar variation permits the introduction of one new variable parameter into the wave function without an additional calculation of the matrix elements. Because of this the accuracy of calculations has been substantially increased especially for a small number of parameters.

We will note that the virial theorem should also be rigorously performed for approximate wave functions obtained by variational /138 method if the scale of length enters into a number of variable parameters. It is fulfilled, in particular, for all approximate atom functions obtained by the Hartree and Fok methods.

§28. The Virial Theorem for the Scattering of Particles by a Central Field. Partial Waves

We will examine the most simple problem concerning the scattering of a flat wave by a spherically symmetrical center of force. After the solution by partial waves, we come to the system of equations (4.5).

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - 2U(r)\right] \psi_k^{(l)}(r) = 0; \quad \psi_k^{(l)}(0) = 0. \quad (1)$$

We will define $\frac{\ell\,(\ell+1)}{r^2} + 2U(r) = V(r)$. We continue to assume that $|r^2\,U(r)| < M$; i.e., it is limited at any given values of r. Then we come to the equation which is general for all values of ℓ

$$\left[\frac{d^2}{dr^2} + k^2 - V(r)\right] \psi_k(r) = 0;\ \psi_k(0) = 0. \tag{2}$$

The solution of this equation for great values of r has the asymptotic form

$$\psi(r) \sim A \sin [kr + \eta(k)]. \tag{3}$$

We will use the variational principle of Hulthen (4.18) and we will conduct a variation on the scale of length in this case. We form the functional

$$I_k(\psi) = \int_0^\infty \psi_k(r) \left[\frac{d^2}{dr^2} + k^2 - V(r)\right] \psi_k(r)\, dr \tag{4}$$

and we shall substitute in it $\psi_k(r)$ for $\psi_k(r + \epsilon r)$. Hereby, the asymptotic behavior of the function

$$\psi_k(r + \epsilon r) \sim A \sin [(k + \epsilon k)\, r + \eta(k)]. \tag{5}$$

is changed. If such a function is substituted in the functional then the integral will diverge. In order to ensure its convergence, it /139 is necessary to substitute in the functional k for $k + \epsilon k$. We obtain

$$I' = \int_0^\infty \psi_k(r + \epsilon r) \left[\frac{d^2}{dr^2} + (k + \epsilon k)^2 - V(r)\right] \psi_k(r + \epsilon r)\, dr =$$

$$= \int_0^\infty \psi_k(\rho) \left[(1 + \epsilon)^2 \frac{d^2}{d\rho^2} + (1 + \epsilon)^2 k^2 - V\left(\frac{\rho}{1 + \epsilon}\right)\right] \psi_k(\rho) \frac{d\rho}{1 + \epsilon} =$$

$$= \int_0^\infty \psi_k(\rho) \left[(1+\epsilon) \left(-\frac{d^2}{d\rho^2} + k^2 \right) - \frac{1}{1+\epsilon} V\left(\frac{\rho}{1+\epsilon} \right) \right] \psi_k(\rho)\, d\rho =$$

$$= \int_0^\infty \psi_k^2(\rho) \left[(1+\epsilon)\, V(\rho) - \frac{1}{1+\epsilon} V\left(\frac{\rho}{1+\epsilon} \right) \right] d\rho. \qquad (6)$$

We lay out the subintegral function in a series by degrees of ϵ and disregard the numbers which are proportional to the square and to the higher degrees of ϵ,

$$(1+\epsilon)\, V(\rho) - \frac{1}{1+\epsilon} V\left(\frac{\rho}{1+\epsilon} \right) =$$

$$= V + \epsilon V - (1 - \epsilon + \cdots)\, V(\rho - \epsilon\rho + \cdots) =$$

$$= V + \epsilon V - V + \epsilon V + \epsilon\rho V' = 2\epsilon V + \epsilon\rho V'. \qquad (7)$$

By substituting the integral ρ for r we have

$$I' = \epsilon \int_0^\infty \psi_k^2 \left(2V + r \frac{dV}{dr} \right) dr. \qquad (8)$$

On the other hand the integrai I' can be examined as a functional $I_{k+\epsilon k}$ in which is substituted the variational function

$$\tilde{\psi} = \psi_k(r + \epsilon r) = \psi_{k+\epsilon k}(r) + \delta\psi. \qquad (9)$$

The function $\psi_{k+\epsilon k}(r)$ has the asymptotic form

$$\psi_{k+\epsilon k}(r) \sim A \sin [(k + \epsilon k)\, r + \eta (k + \epsilon k)]; \qquad (10)$$

and thus

$$\eta(k) = \eta(k + \epsilon k) + \delta\eta, \qquad (11)$$

$$\delta\eta = - \epsilon k \frac{d\eta}{dk} . \qquad (12)$$

By utilizing the variational principle (4.18), we obtain /140

$$I' = A^2 \epsilon k^2 \frac{d\eta}{dk} . \qquad (13)$$

By comparing (8) and (13), we have

$$\int_0^\infty \psi_k^2 (r) \left(2V + r \frac{dV}{dr}\right) dr = A^2 k^2 \frac{d\eta}{dk} . \qquad (14)$$

The member $\frac{\ell (\ell + 1)}{r^2}$ which is contained in function V is abbreviated in the brackets under the integral, and we have, thus (Ref. 39)

$$2 \int_0^\infty \psi_k^{(\ell)} (r) \left(2U + r \frac{dU}{dr}\right) \psi_k^{(\ell)} (r) \, dr = A^2 k^2 \frac{d\eta_\ell}{dk} . \qquad (15)$$

Formula (15) is of interest from several viewpoints. In the first place it is similar to formula (12), Section 2, and was obtained analogously. We thus have a generalization of the virial theorem in the case of a continuous spectrum. In the second place by utilizing formulae (14) and (15) we, knowing the function ψ_k (approximately or exactly) when k is fixed, can by means of it determine not only the phase η (k) but also its derivative; i.e., we can determine also the change in phase η (k) in the vicinity of the point k. In the third place it is curious that formula (15) has an identical form for all values of ℓ and ℓ itself does not enter into it openly. Then, since the functions ψ_ℓ or the phase η_ℓ are not directly related to each other, the solution to equation (1) in the case of each ℓ is an independent problem, and only at the very end the various η_ℓ are combined in process of determining the differential and overall effective cross section.

It is likewise interesting that the generalization of the virial theorem or problems of a continuous spectrum is conducted easily and naturally in quantum mechanics, whereas in classical mechanics this is not so simply achieved. This generalization could not formerly be /141

conducted because in classical mechanics a functional which is simultaneously stationary and reduced to zero along a true trajectory, cannot be constructed.

§29. The Most Simple Example

We shall confirm the validity of the verified formula in the most simple example of a rectangular potential well. We will let

$$V(r) = -V_0, \quad r < a; \quad V(r) = 0, \quad r > a, \tag{1}$$

and we shall examine only the s-scattering ($\ell = 0$). If we designate $V_0 = k_0^2$, then equation (28.2) will take the simple form

$$\psi'' + (k^2 + k_0^2)\psi = 0, \quad \psi(0) = 0, \quad r < a,$$

$$\psi = \sin(\sqrt{k^2 + k_0^2}\, r); \quad \psi'' + k^2\psi = 0, \quad r > a,$$

$$\psi = A \sin(kr + \eta). \tag{2}$$

By equating the function and their derivatives where $r = a$, we find A and η

$$\eta = \operatorname{arctg}\left[\frac{k}{\sqrt{k^2 + k_0^2}} \operatorname{tg}(\sqrt{k^2 + k_0^2}\, a)\right] - ka,$$

$$A^2k^2 = k^2 + k_0^2 \cos^2(\sqrt{k^2 + k_0^2}\, a). \tag{3}$$

By differentiating η through k, we will obtain after simple calculations

$$\frac{d\eta}{dk} = \frac{k_0^2 \sin(2\sqrt{k^2 + k_0^2}\, a)}{2\sqrt{k^2 + k_0^2}\,[k^2 + k_0^2 \cos^2(\sqrt{k^2 + k_0^2}\, a)]} - \frac{ak_0^2 \cos^2(\sqrt{k^2 + k_0^2}\, a)}{k^2 + k_0^2 \cos^2(\sqrt{k^2 + k_0^2}\, a)}, \tag{4}$$

$$A^2k^2\frac{d\eta}{dk} = \frac{k_0^2 \sin\left(2a\sqrt{k^2+k_0^2}\right)}{2\sqrt{k^2+k_0^2}} - ak_0^2 \cdot \quad \left(a\sqrt{k^2+k_0^2}\right). \tag{5}$$

During the calculation of the integral it is necessary to take into consideration that

$$V'(r) = k_0^2\,\delta(r-a). \tag{6}$$

This /142

$$\int_0^a \psi^2(r)\left(2V + r\frac{dV}{dr}\right)dr =$$

$$= -2k_0^2\int_0^\infty \sin^2\left(\sqrt{k^2+k_0^2}\,r\right)dr + k_0^2 a\sin^2\left(\sqrt{k^2+k_0^2}\,a\right) =$$

$$= \frac{k_0^2}{2\left(k^2+k_0^2\right)}\sin\left(2\sqrt{k^2+k_0^2}\,a\right) - k_0^2 a\cos^2\left(\sqrt{k^2+k_0^2}\,a\right) =$$

$$= A^2k^2\frac{d\eta}{dk}, \tag{7}$$

which is necessary to prove.

§30. The Derivation of the Virial Theorem Without the Utilization of the Variational Principle

We will now examine the way in which the basic formula (28.14) is obtained, not utilizing obviously the variational principle. For this we will examine the integral

$$I'\int_0^\infty \psi\left(-\frac{\partial^2}{\partial r^2} + k^2 - V\right)\left(r\frac{\partial\psi}{\partial r} - k\frac{\partial\psi}{\partial r}\right)dr. \tag{1}$$

We shall reorganize the subintegral expression by utilizing the equation which the function ψ satisfies. We have

$$\left(\frac{\partial^2}{\partial r^2} + k^2 - V\right)\psi = 0; \quad \left(\frac{\partial^2}{\partial r^2} + k^2 - V\right)\frac{\partial\psi}{\partial k} + 2k\psi = 0;$$

$$\left(\frac{\partial^2}{\partial r^2} + k^2 - V\right) k\frac{\partial\psi}{\partial k} = -2k^2\psi; \quad \left(\frac{\partial^2}{\partial r^2} + k^2 - V\right)\frac{\partial\psi}{\partial r} = \frac{\partial V}{\partial r}\psi; \qquad (2)$$

$$\left(\frac{\partial^2}{\partial r^2} + k^2 - V\right)\left(r\frac{\partial\psi}{\partial r} - k\frac{\partial\psi}{\partial k}\right) = 2\frac{\partial^2\psi}{\partial r^2} + r\frac{dV}{dr}\psi + 2k^2\psi =$$

$$= \left(2V + r\frac{dV}{dr}\right)\psi.$$

Thus, the integral (1) coincides with the right member of equation (28.14).

We shall introduce the designation /143

$$\varphi = r\frac{\partial\psi}{\partial r} - k\frac{\partial\psi}{\partial k}. \qquad (3)$$

It is easy to determine the asymptotic form of the function φ

$$\psi \sim \sin[kr + \eta(k)],$$

$$r\frac{\partial\psi}{\partial r} \sim kr\cos[kr + \eta(k)],$$

$$k\frac{\partial\psi}{\partial k} \sim \left(kr + k\frac{d\eta}{dk}\right)\cos[kr + \eta(k)],$$

$$\varphi \sim -k\frac{d\eta}{dk}\cos(kr + \eta). \qquad (4)$$

In addition, it is obvious that the function φ is reduced to 0 when $r = 0$.

By integrating through the parts twice, we obtain

$$I' = \int_0^\infty \psi \left(\frac{d^2}{dr^2} + k^2 - V\right) \varphi \, dr =$$

$$= (\psi\varphi' - \psi'\varphi) \Big|_0^\infty + \int_0^\infty \varphi \left(\frac{d^2}{dr^2} + k^2 - V\right) \psi \, dr. \qquad (5)$$

The integral in the right number is equal to 0; the member outside the integral is reduced to 0 at a lower limit. By utilizing the asymptotic form of the functions ψ, φ, we obtain

$$(\psi\varphi' - \psi'\varphi)_{r\to\infty} =$$

$$= \Big[\sin(kr + \eta) \cdot k^2 \frac{d\eta}{dk} \sin(kr + \eta) +$$

$$+ k\cos(kr + \eta) \cdot k \frac{d\eta}{dk} \cos(kr + \eta)\Big]_{r\to\infty} =$$

$$= k^2 \frac{d\eta}{dk}, \qquad (6)$$

which is necessary to prove.

It is easy to see that in essence the pace of evidence here is the same as it was in Section 28 although the variational principle /144 is also not utilized directly. The function φ in a given case is proportional to $\delta\psi$ for that particular case of variation which was examined in Section 28.

§31. Certain Identities Related to the Virial Theorem. The Connection Between the Discrete and the Continuous Spectrum

We will examine the equation

$$\psi'' + \lambda\psi = V(r)\,\psi; \quad \psi(0) = 0. \qquad (1)$$

We will let the potential V (r) be such that the equation has a limited solution for any given $\lambda = k^2 > 0$ and only for a certain finite number of negative values

$$\lambda = \lambda_n < 0, \quad n = 1, 2, \cdots, N. \tag{2}$$

We form the function F (r) according to the formula

$$F(r) = \sum_{n=1}^{N} \frac{1}{\lambda_n} \psi_n^2(r) + \int_0^{\infty} \psi_\lambda^2(r) \frac{d\lambda}{\lambda}. \tag{3}$$

Here, ψ_n is standardized for a unit and the functions of their continuous spectrum ψ_λ are standardized for λ; that is, the conditions

$$\int \psi_\lambda(r) \psi_{\lambda'}(r)\, dr = \delta(\lambda - \lambda'); \tag{4}$$

$$\sum_{n=1}^{N} \psi_n(r) \psi_n(r') + \int_0^{\infty} \psi_\lambda(r) \psi_\lambda(r')\, d\lambda = \delta(r - r') \tag{5}$$

are fulfilled.

In (3) we shall proceed from the integration in λ the integration into k

$$\int_0^{\infty} \psi_\lambda^2(r) \frac{d\lambda}{\lambda} = \int_0^{\infty} \varphi_k^2(r) \frac{dk}{k^2}, \tag{6}$$

where φ_k are the standardized wave functions for k. Their asymptotic behavior is easily obtained from a comparison with the function sin kr since the standardization of the functions of a continuous spectrum is dependent only on their asymptotic behavior /145

$$\varphi_k \sim \sqrt{\frac{2}{\pi}} \sin[kr + \eta(k)]. \tag{7}$$

By proceeding to the usual function $\psi_k(r) \sim \sin(kr + \eta)$ $\varphi_k = \sqrt{\frac{2}{\pi}} \psi_k$, we have

$$F(r) = \sum_{n=1}^{N} \frac{1}{\lambda_n} \psi_n^2(r) + \frac{2}{\pi} \int_0^{\infty} \psi_k^2 \frac{dk}{k^2} . \tag{8}$$

We shall now multiply F (r) by $2V(r) + r\frac{dV}{dr}$ and we shall integrate by r

$$\int_0^{\infty} F(r)\,(2V + r\,V')\,dr =$$

$$= \sum_{n=1}^{N} \frac{1}{\lambda_n} \int_0^{\infty} \psi_n^2(r)\,(2V + r\,V')\,dr +$$

$$+ \frac{2}{\pi} \int_0^{\infty} \frac{dk}{k^2} \int_0^{\infty} \psi_k^2\,(2V + r\,V')\,dr. \tag{9}$$

By utilizing both forms of the virial theorem (27.12) and (28.15)

$$\int_0^{\infty} \psi_n^2(r)\,(2V + r\,V')\,dr = 2\lambda_n, \tag{10}$$

$$\int_0^{\infty} \psi_k^2(r)\,(2V + r\,V')\,dr = k^2 \frac{d\eta}{dk} , \tag{11}$$

We have

$$\frac{2}{\pi}\,[N\pi + \eta(\infty) - \eta(0)] = \int_0^{\infty} F(r) \left[2V(r) + r\frac{dV}{dr}\right] dr. \tag{12}$$

However, it is known (Ref. 56) that the change of phase during the change of k from 0 to ∞ equals exactly Nπ where N is the number of combined states (levels of a discrete spectrum). Thus, the left side of equation (12) is equal to zero, and we have /146

$$\int F(r)\,(2V + r\,V')\,dr = 0. \tag{13}$$

The function F (r) is directly related to the Green function for operator $\frac{d^2}{dr^2} - V$

$$G(r, r') = \sum_{n=1}^{N} \frac{1}{\lambda_n} \psi_n(r)\, \psi_n(r') + \int_0^{\infty} \psi_\lambda(r)\, \psi_\lambda(r')\, \frac{d\lambda}{\lambda}. \qquad (14)$$

Herefrom, it is seen that

$$F(r) = G(r, r).$$

Finally, we have

$$\int_0^{\infty} G(r, r)\, (2V + r\, V')\, dr = 0. \qquad (15)$$

This formula is directly related to both forms of the virial theorem. It is valid only in the case of a continuous or a discontinuous spectrum of specific values.

It is curious that for the case of a purely discrete spectrum it is impossible to obtain such a formula. In this case the integral in formula (3) disappears and N will be equal to ∞, respectively, in formula (12), the left side is reduced to ∞, and thus the integral in (15) for a purely discrete spectrum always diverges.

We will now show the way in which the formula combining the integral $\int_0^{\infty} k\eta(k)\, dk$ with the value of the potential V where r = 0 follows from the virial theorem.

An analogous formula was obtained at first by Gelfand and Levitan (Ref. 72) for a corresponding problem of a discrete spectrum. For the problem of a continuous spectrum this formula was obtained by R. Newton (Ref. 73) and was given a more rigorous foundation by L. Faddeyev (Ref. 74).

Since the formula is already derived and rigorously founded, /147 we will only mention the reasoning process which permits it to be connected with the virial theorem.

By integrating both numbers of equation (11) to k, we obtain

$$\int_0^\infty dk \int_0^\infty \psi_k^2 (r) (2V + r V') dr = \int_0^\infty k^2 \frac{d\eta}{dk} dk. \quad (16)$$

The integral in the right part exists obviously only in the case when, with the increase of k, the phase η (k) decreases more rapidly than k^{-2}. It is possible to prove (using for example the expression for a phase in a Born approximation) that in the case of great values of k, the phase usually decreases, as k^{-1}. More accurately

$$\eta (k) = - \frac{1}{2k} \int_0^\infty V (r) dr + 0 (k^{-3}). \quad (17)$$

It is obvious herefrom that if the right part of formula (16) is final, then the following condition should be fulfilled

$$\int_0^\infty V (r) dr = 0. \quad (18)$$

It is obvious that here with the equation

$$\int_0^\infty \left(2V + r \frac{dV}{dr}\right) dr = 0. \quad (19)$$

is also valid. Proceeding to an examination of the left part of formula (16) it is necessary to note first of all, that a change of the integration order in this formula is inadmissible; a transition to the limit $k \to \infty$ should be made after the transition to the limit $r \to \infty$. Otherwise the calculation of the integral $\int_0^\infty \psi_k^2 (r) dk$ yields an infinity, which enters the subintegral expression as a factor, and thus, the integral cannot be calculated by r.

We shall reorganize the left side of the formula (16) utilizing the resolution of the delta-function through the specific functions of the operator $\frac{d^2}{dr^2} - V$ and through the functions sin kr /148

$$\delta(r - r') = \frac{2}{\pi}\int_0^\infty \psi_k(r)\,\psi_k(r')\,dk + \sum_{n=1}^{N} \psi_n(r)\,\psi_n(r'), \qquad (20)$$

$$\delta(r - r') = \frac{2}{\pi}\int_0^\infty \sin kr \sin kr'\,dk.$$

Herefrom, we obtain formally

$$\int_0^\infty \psi_k^2(r)\,dk = \int_0^\infty \sin^2 kr\,dk - \frac{\pi}{2}\sum_{n=0}^{N} \psi_n^2(r) =$$

$$= \frac{\pi}{2}\left[\delta(0) - \sum_{n=1}^{N} \psi_n^2(r)\right], \qquad (21)$$

and the left side of equation (16) is written as follows*

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*Strictly speaking, in order to base such a substitution, it is necessary to indicate that the equation

$$\lim_{K\to\infty} \int_0^\infty \Phi(r)\left[\int_0^K \psi_k^2(r)\,dk + \frac{\pi}{2}\sum_{n=1}^{N} \psi_n^2(r) - \int_0^K \sin^2 kr\,dk\right] dr = 0$$

is fulfilled for the arbitrary values of $\Phi(r)$ from a sufficiently broad class of functions. This equation can be given evidence by investigating the analytical properties of the function $\psi_k(r)$.

$$\int_0^\infty dk \int_0^\infty \sin^2 kr \left(2V + r\frac{dV}{dr}\right) dr -$$

$$- \frac{\pi}{2} \sum_{n=1}^{N} \int_0^\infty \psi_n^2 (r) \left(2V + r\frac{dV}{dr}\right) dr. \qquad (22)$$

If the virial theorem is utilized for a discrete spectrum (10), then the second item in this expression can be written as /149

$$- \pi \sum_{n=1}^{N} \lambda_n. \qquad (23)$$

The first item can be reorganized by utilizing equation (19) and the Dirichlet formula from the theory of the Fourier integral

$$\int_0^\infty dk \int_0^\infty \sin^2 kr \left(2V + r\frac{dV}{dr}\right) dr =$$

$$= \lim_{K\to\infty} \int_0^\infty \left(2V + r\frac{dV}{dr}\right) dr \int_0^K \sin^2 kr\, dk =$$

$$= \lim_{K\to\infty} \int_0^\infty \left(2V + r\frac{dV}{dr}\right)\left(\frac{K}{2} - \frac{\sin 2Kr}{4r}\right) dr =$$

$$= - \frac{1}{4} \lim_{K\to\infty} \int_0^\infty \left(2V + r\frac{dV}{dr}\right) \frac{\sin Kr}{r} dr = - \frac{\pi}{4} V(0). \qquad (24)$$

By utilizing (16), (22), (23), (24), we obtain

$$\int_0^\infty k^2 \frac{d\eta}{dk} dk = - \frac{\pi}{4} V(0) - \pi \sum_{n=1}^{N} \lambda_n. \qquad (25)$$

By integrating the left side of this equation to the members and by noticing that the number outside the integral $k^2\eta$ is reduced to 0 when $k = 0$ and $k = \infty$, we finally obtain

$$\frac{2}{\pi}\int_0^\infty k\eta\, dk = \frac{1}{4} V(0) + \sum_{n=1}^{N} \lambda_n. \tag{26}$$

In the case where an integral from V (r) is not 0, we can obtain an analogous formula if we note page 150. First of all, subtract from both sides of the equation (11) $\frac{1}{2}\int_0^\infty V(r)\, dr$, and only after this /150 integrate to k.

Then, by having repeated the calculations, we come to the formula

$$\frac{2}{\pi}\int_0^\infty k\left[\eta + \frac{1}{2k}\int_0^\infty V(r)\, dr\right] dk = \frac{1}{4} V(0) + \sum_{n=1}^{N} \lambda_n. \tag{27}$$

In the derivation of these formulae, we assume that $\ell = 0$; that is, that the potential V decreases when $r \to \infty$ faster than r^{-2}. The generalization of the formulae in the case of $\ell \neq 0$ is present in the work (Ref. 73) and does not present any complications in principle.

§32. The Case of a Field Which has the Coulomb Character at Infinity

This case requires special consideration. We will consider that in equation (28.2) the potential V contains the Coulomb member [see (5.2)]

$$V(r) = \frac{c}{r} + v(r), \tag{1}$$

where v (r) decreases at ∞ no less rapid than r^{-2}. Then in the case of fixed c and k the solution to the equation will have the asymptotic form of (5.6)

$$\psi_{k,\,c}(r) \sim \sin\left[kr - \frac{c}{2k}\ln kr + \eta(k, c)\right]. \tag{2}$$

If we now vary the scale in the functional $I_{kc}(\psi)$, we obtain

$$\psi_{kc}(r + \epsilon r) \sim \sin\left[(k + \epsilon k)\, r - \frac{c}{2k} \ln k\,(r + \epsilon r) + \eta(c, k)\right] =$$

$$= \sin\left[(k + \epsilon k)\, r - \frac{c + \epsilon c}{2(k + \epsilon k)} \ln (k + \epsilon k)\, r + \eta(c, k)\right]. \qquad (3)$$

Here it is seen that in the functional I' it is necessary to substitute not only k for $k + \epsilon k$, but also c for $c + \epsilon c$. Only in this case will the functional remain convergent. We obtain /151

$$I' = \int_0^\infty \psi_{kc}(r + \epsilon r)\left[\frac{d^2}{dr^2} + (k + \epsilon k)^2 - \frac{c + \epsilon c}{r} - \right.$$

$$\left. - v(r)\right] \psi_{kc}(r + \epsilon r)\, dr = \int_0^\infty \psi_{kc}(\rho)\left[\left(\frac{d^2}{d\rho^2} + k^2 - \right.\right.$$

$$\left.\left. - \frac{c}{\rho}\right)(1 + \epsilon) - \frac{1}{1 + \epsilon} v\left(\frac{\rho}{1 + \epsilon}\right)\right] \psi_{kc}(\rho)\, d\rho =$$

$$= \epsilon \int_0^\infty \psi_{kc}^2(r)\,[2v(r) + rv'(r)]\, dr + 0(\epsilon^2). \qquad (4)$$

We now utilize the variational principle derived in Section 5

$$I' = I_{k + \epsilon k,\, c + \epsilon c}\left[\psi_{k + \epsilon k,\, c + \epsilon c}(r) + \delta\psi\right] = - k\delta\eta; \qquad (5)$$

$$\psi_{k + \epsilon k,\, c + \epsilon c}(r) \sim \sin\left[(k + \epsilon k)\, r - \frac{c + \epsilon c}{2(k + \epsilon k)} \ln (k + \epsilon k)\, r + \right.$$

$$\left. + \eta(k + \epsilon k, c + \epsilon c)\right]; \qquad (6)$$

$$\eta(k, c) = \eta(k + \epsilon k, c + \epsilon c) + \delta\eta; \qquad (7)$$

$$\delta\eta = -\epsilon\left(c\frac{\partial\eta}{\partial c} + k\frac{\partial\eta}{\partial k}\right). \qquad (8)$$

From (4), (5), and (8) we have

$$\int_0^\infty \psi_{kc}^2(r)\left[2v(r) + r\frac{dv}{dr}\right]dr = kc\frac{\partial\eta}{\partial c} + k^2\frac{\partial\eta}{\partial k}. \qquad (9)$$

In comparison with (15.3) this formula is less suitable for practical calculations, since it contains the value $\frac{\partial\eta}{\partial c}$, which is of considerable lesser interest than $\frac{\partial\eta}{\partial k}$.

We will note that for related states the presence of Coulomb members does not change the formulation of the virial theorem since the asymptotic behavior of the wave function at great distances from the nucleus does not substantially change.

§33. The Variation of Scale in a Three Dimensional Case for Problems of Scattering /152

We consider the equation

$$[\nabla^2 + k^2 - V(\vec{r})]\,\Psi(\vec{r}) = 0. \qquad (1)$$

It is necessary, in this case, to understand the variational principle of Kohn, which was investigated in Section 6, and conduct a variation of scale in the functional (6.8), (6.17)

$$I_k(\Psi_2\,\Psi_1) = \int \Psi_2(\vec{r}, k)\,[\nabla^2 + k^2 - V(\vec{r})]\,\Psi_1(\vec{r}, k)\,d\tau. \qquad (2)$$

We will produce a substitution

$$\Psi_1(\vec{r}, k) \to \Psi_1(\vec{r} + \epsilon\vec{r}, k);\ \Psi_2(\vec{r}, k) \to \Psi_2(\vec{r} + \epsilon\vec{r}, k). \qquad (3)$$

The asymptotic form of the functions Ψ_1, Ψ_2 changes hereby

$$\Psi_i(\vec{r} + \epsilon\vec{r}, k) \sim e^{i(k+\epsilon k)\vec{v}\cdot\vec{r}} + f_k(\vec{v}_i, \vec{n})\frac{e^{i(k+\epsilon k)r}}{(k+\epsilon k)r}. \qquad (4)$$

In order to assure the conversions, we will replace k for $k + \epsilon k$ in the functional (2). We obtain

$$I' = \int \Psi_2 (\vec{r} + \epsilon\vec{r}, k) \times$$

$$\times [\nabla^2 + (k + \epsilon k)^2 - V (\vec{r})] \Psi_1 (\vec{r} + \epsilon\vec{r}, k) d\tau. \quad (5)$$

We will act in approximately the same way as we did in Section 28: we will substitute $\vec{r} + \epsilon\vec{r}$ for $\vec{\rho}$ and utilize equation (1)

$$I' = \int \Psi_2 (\vec{\rho}, k) \left[\frac{1}{1 + \epsilon} (\nabla_\rho^2 + k^2) - \right.$$

$$\left. - \frac{1}{(1 + \epsilon)^3} V \left(\frac{\vec{\rho}}{1 + \epsilon} \right) \right] \Psi_1 (\vec{\rho}, k) d\tau_\rho =$$

$$= \int \Psi_2 (\vec{r}, k) \left[\frac{1}{1 + \epsilon} V (\vec{r}) - \frac{1}{(1 + \epsilon)^3} V \left(\frac{r}{1 + \epsilon} \right) \right] \Psi_1 (\vec{r}, k) d\tau; \quad (6)$$

$$d\tau = \frac{d\tau_\rho}{(1 + \epsilon)^3}; \quad \nabla^2 = (1 + \epsilon)^2 \nabla_\rho^2 .$$

We will lay out the subintegral expression in a row in degrees/153

$$\frac{1}{1 + \epsilon} V (\vec{r}) - \frac{1}{(1 + \epsilon)^3} V \left(\frac{\vec{r}}{1 + \epsilon} \right) =$$

$$= (1 - \epsilon) V (\vec{r}) - (1 - 3\epsilon) (V - \vec{r} \cdot \nabla V) + 0 (\epsilon^2) =$$

$$= 2\epsilon V (\vec{r}) + \epsilon\vec{r} \cdot \nabla V (\vec{r}) + 0 (\epsilon^2). \quad (7)$$

By examining I' as the varied functional $I_{k + \epsilon k} (\tilde{\Psi}_2, \tilde{\Psi}_1$, we have

$$\tilde{\Psi}_1 = \Psi_1 (\vec{r} + \epsilon\vec{r}, k) = \Psi_1 (\vec{r}, k + \epsilon k) + \delta\Psi_1;$$

$$\tilde{\Psi}_2 = \Psi_2 (\vec{r} + \epsilon\vec{r}, k) = \Psi_2 (\vec{r}, k + \epsilon k) + \delta\Psi_2. \quad (8)$$

Herefrom

$$\delta f_2 = - \epsilon k \frac{\partial f_2}{\partial k} .$$

And finally from the variational principle (6.16), we obtain (Ref. 39)

$$\int \Psi_2 (\vec{r}) \left[2V (\vec{r}) + \vec{r} \cdot \nabla V (\vec{r})\right] \Psi_1 (\vec{r}) \, d\tau = 4\pi \frac{\partial f_k (\vec{v}_1, - \vec{v}_2)}{\partial k} \qquad (?)$$

Thus, we have obtained a virial theorem for the general problem of scattering by a potential field.

§34. The Relation of One Dimensional and Three Dimensional Cases (Ref. 39)

In Section 33 we made no assumptions concerning the symmetry of the potential $V (\vec{r})$. Let us now assume that the field is central and the potential is dependent only on r. Then

$$\vec{r} \cdot \nabla V (\vec{r}) = r \frac{dV}{dr} . \qquad (1)$$

We will show that the one dimensional formulation of the virial theorem (28.15) given exactly for the case of the central field follows from the three dimensional (33.9). For this purpose, we will analyze the wave functions and scattering amplitudes by these spherical functions or partial waves. Then [see (4.3, (4.4)] /154

$$f_k (\vec{v}_1, - \vec{v}_2) = \frac{1}{2i} \sum_{\ell=0}^{\infty} (2\ell + 1) \left[e^{2i\eta_\ell} - 1\right] P_\ell (\vec{v}_1, - \vec{v}_2); \qquad (2)$$

$$\Psi_1 = \sum_{\ell=0}^{\infty} (2\ell + 1) \, i^\ell \, e^{i\eta_\ell} \frac{1}{kr} \psi_\ell (r) \, P_\ell (\vec{v} \cdot \vec{n}),$$

$$\Psi_2 = \sum_{\ell=0}^{\infty} (2\ell + 1) \, i^\ell \, e^{i\eta_\ell} \frac{1}{kr} \psi_\ell (r) \, P_\ell (\vec{v}_2 \cdot \vec{n}). \qquad (3)$$

Furthermore

$$P_\ell(\vec{v}_1, -\vec{v}_2) = (-)^\ell P_\ell(\vec{v}_1 \cdot \vec{v}_2). \tag{4}$$

Let us differentiate (2) through k. Thereby, in the right side only the phases η_ℓ are dependent on k

$$4\pi \frac{\partial f_k(\vec{v}_1, -\vec{v}_2)}{\partial k} = 4\pi \sum_{\ell=0}^{\infty} (2\ell + 1)\, e^{2i\eta_\ell} \cdot \frac{d\eta_\ell}{dk} (-)^\ell P_\ell(\vec{v}_1 \cdot \vec{v}_2). \tag{5}$$

Let us substitute, in the left side of equation (33.9), Ψ_1 and Ψ_2 in the form (3). By utilizing the orthogonality of the spherical functions, we have

$$\frac{1}{k^2} \sum_{\ell,\ell'=0}^{\infty} \left\{ \int_0^\infty \psi_\ell(r) \left[2V(r) + r\frac{dV}{dr}\right] \psi_{\ell'}(r)\, dr \cdot i^{\ell+\ell'} e^{i(\eta_\ell + \eta_{\ell'})} \times \right.$$

$$\left. \times (2\ell + 1)(2\ell' + 1) \int P_\ell(\vec{v}_2 \cdot \vec{n})\, P_{\ell'}(\vec{v}_1 \cdot \vec{n})\, d\omega \right\} =$$

$$= \frac{1}{k^2} \sum_{\ell=0}^{\infty} \left[\int_0^\infty \psi_\ell(r) \left(2V + r\frac{dV}{dr}\right) \psi_\ell(r)\, dr \times \right.$$

$$\left. \times \int P_\ell(\vec{v}_2 \cdot \vec{n}) \cdot P_\ell(\vec{v}_1 \cdot \vec{n})\, d\omega\, (2\ell + 1)^2 (-)^\ell e^{2i\eta_\ell} \right]. \tag{6}$$

Furthermore, by utilizing the addition theorem (9.4), we obtain /155

$$\int \Psi_2 [2V(r) + \vec{i} \cdot \nabla V(r)] \Psi_1 d\tau = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1)\, e^{2i\eta_\ell} \times$$

$$\times (-)^\ell P_\ell(\vec{v}_1 \cdot \vec{v}_2) \int_0^\infty \psi_\ell^2(r)\, (2V + rV')\, dr. \tag{7}$$

By substituting (5) and (8) in formula (33.9) of the preceding section and by comparing the members for the case of identical values of P_ℓ, we obtain actually a one dimensional formulation of the virial theorem (28.15).

Let us note that all formulae which are examined here (and, in particular, both formulations of the virial theorem) are applicable not only in quantum mechanics but also for any given problem which is described by equation (33.1); that is, for a problem concerning the defraction of a flat wave on spatial inhomogeneity of finite dimensions.

The derivation of these formulae has a certain similarity to the derivation of the virial theorem for molecules. Here, during the variation of scale, it is necessary to change the wave number; therefore, the derivative of the phase or scattering amplitude by wave number enters into the finite formula. In the case of a molecule the variation of scale changes the distance between nuclei and the derivative of the overall energy of the molecule enters into a finite formula according to the distance between the nuclei (in an equilibrium position of the molecule this derivative is reduced to 0).

§35. Variational Methods and the Scattering of Electrons on the Thomas-Fermi Atom

The problem concerning the scattering of electrons on the neutral atom with an arbitrary charge in the nucleus Z can be approximately solved if we examine the atom in the Thomas-Fermi method. In this case, it is necessary to substitute the atom by means of the center of force with a potential calculated from the Thomas-Fermi equation, which is expressed through one universal function for any given Z

$$U_Z(r) = -\frac{Z}{r}\,x\left(\frac{r}{b}\,Z^{1/3}\right), \tag{1}$$

where /156

$$b = 0.885 = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3},$$

and x (x) satisfies the equation

$$x'' = x^{1/2}x^{3/2}; \quad x(0) = 1, \quad x(\infty) = 0. \tag{2}$$

The scattering of electrons on the atom is described in this approximation by the equation

$$\left[\nabla^2 + k^2 + \frac{2Z}{r} \varkappa \left(\frac{r}{b} Z^{1/3}\right)\right] \Psi (\vec{r}) = 0. \tag{3}$$

The wave function Ψ should have the asymptotic form

$$\Psi (k, Z; \vec{r}) \sim e^{ik\vec{v}\cdot\vec{r}} + f_{kZ} (\vec{v} \cdot \vec{n}) \frac{e^{ikr}}{kr} . \tag{4}$$

The problem is concluded in finding $f_{kZ} (\vec{v} \cdot \vec{n})$.

However, in this organization the problem is solved quite roughly (in particular, we disregard the exchange and polarization of the atom by a bombarding electron). It is still possible to obtain satisfactory accord with an experiment even for slow electrons except when their scattering occurs on great angles. The Thomas-Fermi potential yields a poor estimation of the true distribution of electrons with large values of r; therefore, the electron scattering on small angles (which occurs primarily during "distant" collisions) does not yield conformity with the experiment.

Equation (3) is easily solved in a Born approximation. In this case, we obtain (Ref. 36)

$$f_{kZ} (\cos \theta) = kZ^{2/3} \varphi \left(kb \sin \frac{\theta}{2} \cdot Z^{-1/3}\right) , \tag{5}$$

and thus, in this approximation, f is expressed through one universal function for all values of k, Z and θ.

However, generally speaking, this formula is already illogical with small values of k and equation (3) must be solved for each value of k and Z (Ref. 1).

Let us look at the types of general formulae which can be obtained in this case by using the variational principle. The functional (6.17) will have the form /157

$$I_{kZ} [\Psi_2 (k, Z; \vec{r}); \Psi_1 (k, Z; \vec{r})] =$$

$$= \int \Psi_2 \left[\nabla^2 + k^2 + \frac{2Z}{r} \varkappa \left(\frac{r}{b} Z^{1/3}\right)\right] \Psi_1 \, d\tau . \tag{6}$$

A variation of the scale on this functional leads as usual to a formulation of the virial theorem for the given case

$$- 2 \int \Psi_2 \left[2 \frac{Z}{r} x \left(\frac{r}{b} Z^{4/3} \right) + r \frac{d}{dr} \frac{Z}{r} x \left(\frac{r}{b} Z^{1/3} \right) \right] \Psi_1 \, d\tau =$$

$$= 4\pi \frac{\partial f}{\partial k} . \qquad (7)$$

By simplifying the expression in the quadratic brackets, we have

$$- 2 \int \Psi_2 \left[\frac{Z}{r} x \left(\frac{r}{b} Z^{1/3} \right) + \frac{1}{b} Z^{4/3} x' \left(\frac{r}{b} Z^{1/3} \right) \right] \Psi_1 \, d\tau =$$

$$= 4\pi \frac{\partial f}{\partial k} . \qquad (8)$$

However, other than the variation of scale, it is possible to conduct in this functional another variation of charge in the nucleus Z. Let us substitute in the functional (6) Z for $Z + \epsilon Z$, leaving Ψ_1, Ψ_2 unchanged. Then it is possible to write

$$I_{k, Z+\epsilon Z} (\Psi_2, \Psi_1) = I_{k, Z+\epsilon Z} [\Psi_2 (k, Z + \epsilon Z; \vec{r}) + \delta\Psi_2,$$

$$\Psi_1 (k, Z + \epsilon Z; \vec{r}) + \delta\Psi_1]. \qquad (9)$$

hereby

$$\delta f (\vec{v}_1, - \vec{v}_2) = \delta f (- \cos \theta) = - \epsilon Z \frac{\partial f}{\partial Z} . \qquad (10)$$

By using a variational principle, we have

$$I_{k, Z+\epsilon Z} (\Psi_2, \Psi_1) = \frac{4\pi}{k} \epsilon Z \frac{\partial f}{\partial Z} + O (\epsilon^2). \qquad (11)$$

On the other hand /158

$$I_{k,Z+\epsilon Z}(\Psi_2, \Psi_1) =$$

$$= \int \Psi_2 \left\{\nabla^2 + k^2 + \frac{2(Z+\epsilon Z)}{r} x\left[(1+\epsilon)^{1/3} \cdot \frac{r}{b} Z^{1/3}\right]\right\} \Psi_1 \, d\tau =$$

$$= 2\epsilon \int \Psi_2 \left[\frac{Z}{r} x\left(\frac{r}{b} Z^{1/3}\right) + \frac{1}{3b} Z^{4/3} x\left(\frac{r}{b} Z^{1/3}\right)\right] \Psi_1 \, d\tau +$$

$$+ O(\epsilon^2). \qquad (12)$$

Thus, we have two very similar formulae

$$2k \int \Psi_2 \left[\frac{Z}{r} x\left(\frac{r}{b} Z^{1/3}\right) + \frac{1}{b} Z^{4/3} x'\left(\frac{r}{b} Z^{1/3}\right)\right] \Psi_1 \, d\tau =$$

$$= -4\pi k \frac{\partial f}{\partial k}; \qquad (8)$$

$$2k \int \Psi_2 \left[\frac{Z}{r} x\left(\frac{r}{b} Z^{1/3}\right) + \frac{1}{3b} Z^{4/3} x'\left(\frac{r}{b} Z^{1/3}\right)\right] \Psi_1 \, d\tau =$$

$$= 4\pi Z \frac{\partial f}{\partial Z}. \qquad (13)$$

Definitely the same type of formulae can be obtained also for partial waves

$$\frac{2}{k} \int_0^\infty \varphi_\ell^2(r) \left[\frac{Z}{r} x\left(\frac{r}{b} Z^{1/3}\right) + \frac{1}{b} Z^{4/3} x'\left(\frac{r}{b} Z^{1/3}\right)\right] dr =$$

$$= -k \frac{\partial \eta_\ell}{\partial k}; \qquad (14)$$

$$\frac{2}{k} \int_0^\infty \varphi_\ell^2(r) \left[\frac{Z}{r} x\left(\frac{r}{b} Z^{1/3}\right) + \frac{1}{3b} Z^{4/3} x'\left(\frac{r}{b} Z^{1/3}\right)\right] dr =$$

$$= Z \frac{\partial \eta_\ell}{dZ}. \qquad (15)$$

Here ψ_ℓ is the radio functions of the ℓ-th partial wave.

It is also obvious from the considered example, that if the energy operator H, in the case of a certain problem in the collision theory, contains a parameter, the variation of which changes scattering amplitude in the asymptotic form of the wave function only, then we can easily/159 obtain an expression for the derivative from the phase or scattering amplitude along this parameter, by utilizing the variational principle. This assertion follows directly from the fact that the scattering amplitude and the phase are stationary values of some functionals.

§36. The Virial Theorem and the Born Method

Let us explain the aspect that formulae (28.14) and (33.9) will have in the presence of great values of k when the Born approximation is valid. For the problem concerning the scattering of particles by the center of force, we have the following approximate expression for the phases (10.37)

$$\eta_\ell = -\frac{\pi}{2}\int_0^\infty V(r)\left[I_{\ell+1/2}(kr)\right]^2 r\,dr. \tag{1}$$

The approximate solution to the equation for the radio functions is

$$\psi_\ell'' + \left[k^2 - \frac{\ell(\ell+1)}{r^2} - V(r)\right]\psi_\ell = 0; \quad \psi(0) = 0, \tag{2}$$

if V (r) is considered small in comparison with k^2 it is well known (10.34) that

$$\psi_\ell(r) \approx \varphi_\ell(kr) = \left(\frac{\pi kr}{2}\right)^{1/2} I_{\ell+1/2}(kr). \tag{3}$$

These solutions have the asymptotic form

$$\varphi_\ell \sim \sin\left(kr - \frac{\ell\pi}{2}\right). \tag{4}$$

By substituting (3) in (1), we have

$$\eta_\ell = -\frac{1}{k}\int_0^\infty V(r)\,\varphi_\ell^2(kr)\,dr. \tag{5}$$

In order to obtain an equation analogous to formula (28.14), /160 we will differentiate formula (5) through k. We have

$$\frac{d\eta_l}{dk} = \frac{1}{k^2}\int_0^\infty V(r)\,\varphi_l^2(kr)\,dr -$$

$$-\frac{1}{k}\int_0^\infty V(r)\,\frac{\partial}{\partial k}\left[\varphi_l^2(kr)\right]dr. \qquad (6)$$

It is now possible to utilize the fact that the approximate solution to equation (2) φ_l is dependent only on the derivative kr, and we will substitute the differentiation through k by the differentiation through r in the second integral. Actually

$$k\frac{\partial}{\partial k}\varphi_l^2(kr) = r\frac{\partial}{\partial r}\varphi_l^2(kr) = 2kr\varphi_l\varphi_l';$$

$$\frac{\partial}{\partial k}\varphi_l^2 = \frac{r}{k}\frac{\partial}{\partial r}\varphi_l^2. \qquad (7)$$

Let us substitute (7) in (6) and integrate through the parts

$$\frac{d\eta_l}{dk} = \frac{1}{k^2}\int_0^\infty V(r)\,\varphi_l^2 dr - \frac{1}{k^2}\int_0^\infty V(r)\,r\frac{\partial}{\partial r}\varphi_l^2\,dr =$$

$$= \frac{1}{k^2}\int_0^\infty V(r)\,\varphi_l^2 dr + \frac{1}{k^2}\int_0^\infty \varphi_l^2\frac{d}{dr}[r\,V(r)]\,dr =$$

$$= \frac{1}{k^2}\int_0^\infty \varphi_l^2\left(2V + r\frac{dV}{dr}\right)dr. \qquad (8)$$

Thus, in the framework of the Born method, formula (28.14) is fulfilled if, instead of an exact wave function, we substitute an approximate function (3) and calculate the phases according to formula (1).

Analogously it is possible to investigate a general problem of scattering of particles by a field of forces. In this case, the wave functions at great distances from the center of force have the asymptotic form

$$\Psi(\vec{r}) \sim e^{ik\vec{v}\cdot\vec{r}} + f_k(\vec{v}, \vec{n}) \frac{e^{ikr}}{kr}. \quad (9)$$

In the Born approximation $f_k(\vec{v}, \vec{n})$ can be calculated according to /161 formula (10.26).

$$f_k(\vec{v}, \vec{n}) = -\frac{k}{4\pi}\int V(\vec{r})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau. \quad (10)$$

Let us differentiate this equation through k

$$\frac{\partial f}{\partial k} = -\frac{1}{4\pi}\int V(\vec{r})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau -$$

$$-\frac{k}{4\pi}\int V(\vec{r})\frac{d}{dk} e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau. \quad (11)$$

Let us substitute again the differentiation through k in the second integral by the differentiation through the coordinates. We have

$$\frac{d}{dk} e^{ik(\vec{v}-\vec{n})\cdot\vec{r}} = i(\vec{v}-\vec{n})\cdot\vec{r} e^{ik(\vec{v}-\vec{n})\cdot\vec{r}};$$

$$\nabla e^{ik(\vec{v}-\vec{n})\cdot\vec{r}} = ik(\vec{v}-\vec{n})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}};$$

$$\frac{d}{dk} e^{ik(\vec{v}-\vec{n})\cdot\vec{r}} = \frac{1}{k}\vec{r}\cdot\nabla e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}. \quad (12)$$

Thus

$$\frac{\partial f}{\partial k} = -\frac{1}{4\pi}\int V(\vec{r})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau -$$

$$-\frac{1}{4\pi}\int V(\vec{r})\,\vec{r}\cdot\nabla e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau. \quad (13)$$

We utilize the vector identity

$$\operatorname{div}(\varphi\vec{A}) = \varphi \operatorname{div}\vec{A} + \vec{A}\cdot\nabla\varphi \tag{14}$$

and we let

$$\vec{A} = \vec{r}V, \quad \varphi = e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}.$$

then

$$\frac{\partial f}{\partial k} = -\frac{1}{4\pi}\int V(\vec{r})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\, d\tau +$$

$$+\frac{1}{4\pi}\int e^{ik(\vec{v}-\vec{n})\cdot\vec{r}} \operatorname{div}[\vec{r}\, V(\vec{r})]\, d\tau -$$

$$-\frac{1}{4\pi}\int \operatorname{div}\left[\vec{r}\, V(\vec{r})\, e^{ik(\vec{v}-\vec{n})\cdot\vec{r}}\right] d\tau. \tag{15}$$

Furthermore, we have /162

$$\operatorname{div}[\vec{r}\, V(\vec{r})] = V \operatorname{div}\vec{r} + \vec{r}\cdot\nabla V = 3V + \vec{r}\cdot\nabla V. \tag{16}$$

Furthermore, the last integral in formula (15) can be reorganized into a superficial integral and it is reduced to zero at the limit if V decreases rapidly enough. Finally, we obtain

$$4\pi\frac{\partial f(\vec{v},\vec{n})}{\partial k} = \int e^{-ik\vec{n}\cdot\vec{r}}\,[2V(\vec{r}) + \vec{r}\cdot\nabla V(\vec{r})]\, e^{ik\vec{v}\cdot\vec{r}}\, d\tau. \tag{17}$$

Thus, we have obtained formula (33.9) in which flat waves were substituted instead of the functions Ψ_1 and Ψ_2.

§37. The Virial Theorem for the Problem Concerning the Collision of Electrons with an Atom. The Possibility of Applying the Theorem in Numerical Calculation

The case of electron scattering on an atom of hydrogen can be examined exactly the same way as the scattering on the center of force.

In the complete wave function $\Psi(\vec{r}_1, \vec{r}_2)$ it is necessary to vary the scale simultaneously by both arguments. Thus, for instance with great values of r_2, the varied non-symmetrized wave function will have the asymptotic form:

$$\tilde{\Psi}^{(i)} = \Psi^{(i)} + \delta\Psi^{(i)} = \Psi^{(i)}(\vec{r}_1 + \epsilon\vec{r}_1, \vec{r}_2 + \epsilon\vec{r}_2) \sim$$

$$\sim \psi_i(\vec{r}_1 + \epsilon\vec{r}_1)\, e^{ik\vec{v}\cdot(\vec{r}_2 + \epsilon\vec{r}_2)} +$$

$$+ \sum f_{in}(\vec{v}, \vec{n}_2) \frac{e^{ik_n(r_2+\epsilon r_2)}}{k_n(r_2 + \epsilon r_2)} \psi_n(\vec{r}_1 + \epsilon\vec{r}_1). \qquad (1)$$

As can be seen, the appearance of the atomic wave functions likewise changes in an asymptotic resolution. As we see, the appearance of the atomic wave functions in an asymptotic resolution likewise changes. As a result, it is essential to use the variational principle formulated in Section 8, Chapter I where the potential of such a variation is taken into consideration. Furthermore, the argument is conducted in identically the same manner as it was in Section 8, and we come to the formulae

$$\iint \Psi_2^{(j)}(\vec{r}_1, \vec{r}_2)\,(2V + \vec{r}_1 \cdot \nabla_1 V + \vec{r}_2 \cdot \nabla_2 V)\, \Psi_1^{(i)}(\vec{r}_1, \vec{r}_2)\, d\tau_1 d\tau_2 =$$

$$= \frac{4\pi}{k_j} \frac{\partial f_{ij}(\vec{v}_1, -\vec{v}_2)}{\partial k}; \qquad (2)$$

$$\iint \Psi_2^{(j)}(\vec{r}_2, \vec{r}_1)\,(2V + \vec{r}_1 \cdot \nabla_1 V + \vec{r}_2 \cdot \nabla_2 V)\, \Psi_1^{(i)}(\vec{r}_1, \vec{r}_2)\, d\tau_1 d\tau_2 \quad /163$$

$$= \frac{4\pi}{k_j} \frac{\partial g_{ij}(\vec{v}, -\vec{v}_2)}{\partial k}. \qquad (3)$$

The potential V has, for a given problem, the form

$$V = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} \qquad (4)$$

and is a homogeneous function on the order of - 1. Let us utilize the Euler theorem and, in addition, we shall come to the symmetrized functions $\Psi^{\pm}$. Then

$$\frac{1}{2}\iint [\Psi_2^{(j)}(\vec{r}_1, \vec{r}_2) \pm \Psi_2^{(j)}(\vec{r}_2, \vec{r}_1)] V [\Psi_1^{(i)}(\vec{r}_1, \vec{r}_2) \pm$$

$$\pm \Psi_1^{(i)}(\vec{r}_2, \vec{r}_1)] d\tau_1 d\tau_2 =$$

$$= \frac{4\pi}{k_j}\frac{\partial}{\partial k}[f_{ij}(\vec{v}_1, -\vec{v}_2) \pm g_{ij}(\vec{v}_1, -\vec{v}_2)]. \quad (5)$$

If partial waves are considered for this same problem (for instance, the S-wave) then it is possible in the same manner to obtain the formulae for the derivative of the phase. These formulae are analogous to formula (28.15).

The virial theorem, which was proven in this chapter in the case of various problems, may be utilized for the purpose of simplification or confirmation of calculations in the collision theory.

Let us note first of all that the virial theorem will be rigorously fulfilled for phases and wave functions calculated according to the variational method, if the variation of scale enters into the number of variable parameters. This assertion is fulfilled first of all for calculation in the method of a self coordinated field with and without the consideration of exchange (for instance, for the Morse and Allis (Ref. 3) calculation).

Unfortunately, the wave functions obtained as a result of these calculations were not published, and therefore a similar confirmation is impossible.

If the variation of scale did not enter into a number of the variable parameters [as it did, for example, in the work of Massey and Moiseiwitsch (Ref. 21)] then the virial theorem would be fulfilled only approximately. In this case the check can serve as a criterion of accuracy in the method. If the value $\frac{d\eta}{dk}$, which was obtained in the /164 virial theorem is substantially distinct from that which will be received in direct differentiation of the calculated phase η (k), then it is obvious that either of the number of variable parameters is too small or the initial form of the wave function was unsuccessfully selected.

It is also obvious that, if we know the value of the phase simultaneously with its derivative, the number of points which must be taken for the construction of the curve η (k) can be significantly decreased.

Let us note that in the calculation of collisions of an electron with an atom the magnitude $\frac{\partial \eta}{\partial k}$ or the $\frac{\partial f}{\partial k}$ is expressed through a matrix element of the potential energy V, and thus for the determination of these magnitudes no additional calculations are required.

The virial theorem for the scattering of particles by the center of force (Sections 28, 33, 34) was formulated in the work (Ref. 39). A generalization to more complicated problems (Section 37), and likewise certain other results (Sections 31, 32, 35, 36), which were given in this chapter are contained in the dissertation of the author (Ref. 38).

The methods which were examined here were likewise applied in the work of Yu. V. Novozhilov (Ref. 32) for relativistic problems and problems of the quantum theory of field.

CONCLUSION /165

The variational principles in collision theory were formulated comparatively recently and are still only beginning to find application in theoretical reasonings and numerical calculations. However, already it is possible to assert that the variational principles permit the examination of well known facts from a modern point of view. They enable us to obtain a series of new theoretical results by a simpler method and to elaborate on new effective methods of calculation.

In the contents of the book it is seen that almost all divisions of the collision theory are in one way or another related to variational principles; of course, all such divisions have not been examined here. Thus, for example, the investigation of analytical characteristics of the scattering operator, the resonance formula, the behavior of the phase in the case of little energy, the connection between discrete and the continuous spectrum -- all these questions are either directly or indirectly related to variational principles (the Schwinger variational principle, the virial theorem, etc.). To date, many problems have been insufficiently studied and still wait their solution.

That which concerns numerical calculations is the fact that evidently only variational methods permit an effective and rigorous consideration, for example, of such phenomena as polarization of the atom by a bombarding electron and the collection of results, in principle, of the same degree of accuracy achieved in calculation of energy levels of atoms and molecules. In spite of this, experience in the production of such calculations has been accumulated quite slowly. To date in a majority of works either a one dimensional equation for the phase or the equation of the self coordinated field was solved, i.e., those problems which can be solved by different numerical methods especially in the presence of electronic machines. The problem of variational calculations /166 consists, first of all, in the indispensability of extremely exhausting calculations of matrix elements. Of course, this work has with difficulty yielded to mechanization In addition, problems concerning selection of trial functions and convergeability of various methods have been poorly investigated in comparison with the discrete spectrum.

However, these difficulties are surmountable and, thanks primarily to them, investigations in this new region have become of special interest.

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